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THE EFFECT OF SOIL PHYSICAL CONDITIONS ON MOISTURE CONSTANTS IN THE UPPER CAPILLARY RANGE

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U. S. Department of Agriculture

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The physical condition is important in any investigation pertaining to soils. Soils are ordinarily studied either in their natural state or in a derived state produced by fragmenting the natural soil. The textural porosity (that included within an aggregate of primary particles) is identical in either the natural or the fragmented state, since a fragment is a part of an aggregate and has survived the crushing process. The secondary pore space is, however, vastly different. The structural porosity (that included between aggregates) of the natural soil is destroyed during crushing and is replaced by the pore pattern between fragments. Again the physical properties of natural aggregates and mechanically produced fragments are quite different. Likewise, the physical properties of soil systems composed of natural aggregates differ from those of soil systems composed of fragments.

Certain moisture constants in the upper capillary range, such as moisture equivalent, field capacity, and normal moisture capacity, may present different values in the natural state and in the fragmented state. Constants such as these are usually determined on fragmented soils, and the results are assumed to apply equally to all soil conditions, as assumption that is open to doubt. The need for investigation becomes more apparent when certain studies of Bradfield (4) and other workers (10) are examined. These have indicated that size distribution of pores should be directly related to soil structure and to definite physical properties.

The purpose of this paper is to establish the part played by the secondary pore space and to give such physical interpretations as are appropriate. Detailed consideration will be given to moisture equivalent followed by brief discussions of field capacity and normal moisture capacity.

MOISTURE EQUIVALENT

Moisture equivalent of fragmented samples

When the moisture equivalent of a natural soil (one that has not been disturbed by any process to which it was not subjected while in the natural landscape) is to be determined, aggregates of the sample taken are usually crushed to fragments of a size that enables them just to pass a 2-mm. sieve, and all stony material greater than 2 mm. is discarded. The resulting fragments are of two kinds: those wholly nonporous, such as sand and mineral grains, and those which are porous, such as fragments or aggregates from a clayey horizon. A given soil

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sample may reduce to a single one of these types or consist of a mixture of the two.

Characteristic pore-space patterns, depending on the soil, appear in the fragmented soil in a moisture equivalent box. If the sample consists wholly of non-porous grains, as does a sand, only the pore space between the grains exists. On the other hand, if the sample contains porous fragments, then there exists not only the secondary pore space, that between the fragments, but also the textural pore space, that within the fragments. Single porous fragments, for example, those from clayey horizons, have the textural pore space possessed in the natural soil, since each is a fragment of it. The secondary pore space has arisen in the process of preparing the sample.

The relative sizes of the pores, textural and secondary, involved in a given sample are important. For nonporous grains, the size of the pores is of the same order as that of the grains. For samples composed of porous fragments, the size of the textural pores is of the same order as that of the grains, and the size of the capillaries of the secondary pore space is of the same order as that of the fragments themselves.

The final disposition of water will depend on the kind and size of the pore spaces available after the centrifugal field has been applied. With packings of non-porous grains, only slight alterations of the pore space occur. The amount of water retained after application of the centrifugal field will depend on the relative capillary curvatures that can be supported by the pores of the packing and hence on the grain size and porosity.

With samples composed of porous fragments, however, conditions are more complicated. If the fragments are not deformable, then both the textural and secondary pore spaces may support capillary curvatures, and the amount of water in each will depend on their relative sizes. If however, they are deformable, as is usually the case with a clayey soil, most of the secondary pore space disappears when the sample is centrifuged, leaving as the chief water reservoir only the textural pore space, which has a magnitude nearly equal to that existing in the unfragmented soil. The approximate drainage behavior for a packing of non-porous grains is shown in figure 1; that for a packing of porous grains is shown in figure 2.²

² Figures 1 and 2 are obtained from considerations on what happens in the capillary systems, particularly the textural and secondary, when saturated with water and subjected to the action of the centrifugal field. It will be observed that, initially, moisture equivalent samples are thoroughly soaked, and the maximum of water is taken up. The entire pore space is then saturated (saturation probably is not complete in any actual case, because of trapped air and the like), and all other capacities for taking up water, such as arise from organic matter or clay minerals like montmorillonite (lattice water), have been satisfied. Only the capillary water, resting as it does in the pore space, will be considered here. Detailed consideration will be given to two cases; viz., nonporous fragments and porous fragments.

With completely nonporous fragments the behavior is like that shown in figure 1. In this figure, *a* is a scale plot from scattered experimental data; *b* is a schematic diagram based on *a* and exaggerated for the purpose of this discussion. Only one type of pore space, a textural one, is present. At low fields little water leaves the sample (arc *BC* of figure 1*b*,

Figure 3a shows the postulated location of water at the moisture equivalent in the pore space of a sand. Figure 3b shows the corresponding case for porous aggregates. An attempt has been made, in the drawings, to keep capillary curvatures the same for both cases.

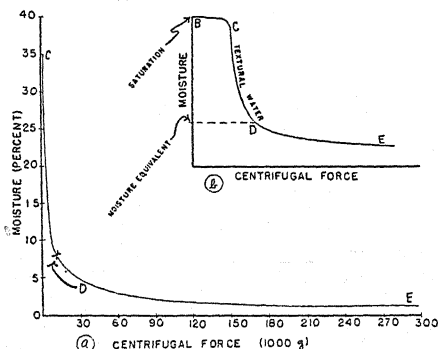


FIG. 1. MOISTURE RETAINED IN A SAND, REPRESENTED AS A FUNCTION OF THE APPLIED CENTRIFUGAL FIELD

a, actual data; *b*, schematic diagram

The fact that hysteresis in moisture equivalent measurements is not to be expected from simple capillary effects, may be easily shown. Ordinarily this phenomenon occurs in cycles of wetting and drying. Figure 3b illustrates capillary hysteresis in spheres. On drying, starting from complete saturation, only

which may be very small, depending on the size of the largest pores). When, however, a field sufficiently great is reached to overcome the capillary forces existing at the continuous meniscus enclosing the sample, water drains (arc *CD*, fig. 1b), leaving within the soil only isolated funicular and pendular bodies. As the field further increases (arc *DE*, figure 1b), the funicular water (isolated bodies of water enmeshed in small grain clusters and completely filling each cluster) drains, and pendular masses remain at the higher fields.

The weight of water remaining at 1000 gravity, per gram of soil, characterizes moisture equivalent. The type of water remaining at this field will depend upon the curvatures of the capillary surfaces which can be supported by the soil framework and exist in equilibrium with the field. Thus the moisture equivalent of a soil depends upon the pore size distribution, which in turn depends upon the texture and compaction of the soil. With coarse sand the residual water is chiefly pendular. With finer texture more funicular water remains. Finally, if the texture is sufficiently fine, the field of 1000 gravity may not be sufficient to overcome the capillary forces existing when the soil is saturated, and the sample will remain completely filled. Thus, the moisture equivalent of quartz flour of silt size is 25 per cent (12). When, however, a field of 300,000 gravity (centrifugal moisture) is reached, the moisture content by weight (grams of water per gram of soil) is only 1.2 per cent (12). The latter value corresponds to the moisture equivalent of coarse sands (20-30 mesh) where only pendular water remains. The point *D*, which indicates moisture equivalent, is not fixed on the curve of figure 1b, but may be anywhere along the curve *CDE*, depending upon the texture. The arc *CD* of figure 1a has been slightly displaced; otherwise it would be indistinguishable from the axis of ordinates for the scale used.

With porous fragments the behavior is more complicated and is probably as indicated in fig. 2. The larger diagram, *a*, is plotted, except for the arc *ABC*, from the data of Olmstead (12); *A* is an experimental point, the arc *BC* is conjecture and not experimental, but is drawn

the curvatures B will exist for the vapor pressures near the moisture equivalent. If, on the other hand, the soil is wetted, then the curvatures C inside aggregate 1

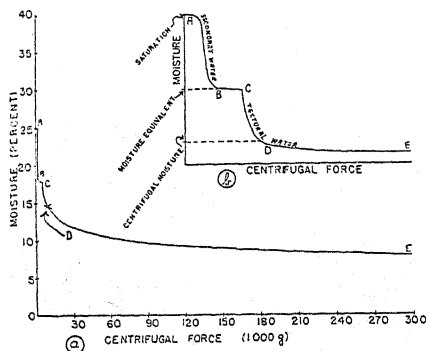


FIG. 2. MOISTURE RETAINED IN A FRAGMENTED HEAVY SOIL, REPRESENTED AS A FUNCTION OF THE APPLIED CENTRIFUGAL FIELD

a , actual data; b , schematic diagram. The arc BC of a would escape detection in most cases may exist, leaving the interior of the aggregate incompletely filled. The curvatures B and C will have the same value and hence the same vapor pressure. The water content of the aggregate will be different in each case. This is an example

in the form it is believed should exist if the effect under discussion could be isolated and not masked. The smaller diagram, b , is again an exaggerated representation of curve a and will, as before, be used exclusively for the immediate discussion.

The following behavior is indicated: The point of initial saturation is shown at A , where both secondary and textural pore spaces are filled. Water does not leave the sample in appreciable quantities until a field sufficiently strong to overcome the capillary forces exerted by the liquid in the secondary pore space is reached. The liquid in this space then empties along the curve AB .

The capillaries of the secondary pore space are the largest of the packing and are of the order of the fragments in size. The fragments, when wet, are deformable and will pack under the field; hence the secondary pore space disappears as the field increases. A small part of it probably remains after a field of 1000 gravity is reached. Observation of the volume changes and compaction which heavy soils placed in a moisture-equivalent box undergo when centrifugation tends to confirm this belief. The secondary pore space empties and disappears as centrifugation progresses. Because of the destruction of this pore space, the arc BC would probably be undetectable at the conclusion of centrifuging. The curve $ABCDE$ would be smooth and without a cusp at C . Each single fragment is, however, saturated. No further loss of moisture, with increase of field, occurs until a field is reached (C in figure 2) sufficient to overcome the capillary forces arising from the continuous meniscus enclosing each fragment.

The textural capillaries, being much finer than those of the secondary pore space, require a much greater field to remove water from them, and they remain saturated until such field is reached. Water leaves the textural pore space of the fragments along the arc CD and it is probably well removed when the point D is reached. This, according to Olmstead (12), is, for some soils, about 30,000 gravity. Beyond D , extremely large fields remove but little of the remaining water. The process of removal, from the fragments, of the textural water held by capillary forces, is similar to its removal from a coarse sand. Both funicular and pendular water remain, and the amount of each depends upon the field applied. Thus the arc $BCDE$ of figure 2 is similar to the arc $BCDE$ of figure 1.

of microscopic hysteresis (17). Moisture equivalent determinations are essentially drying processes, starting from saturation.

If all pores of the soil are completely filled, the porosity, P , may easily be obtained from the moisture equivalent M . If ρ is the density of soil solids, and d

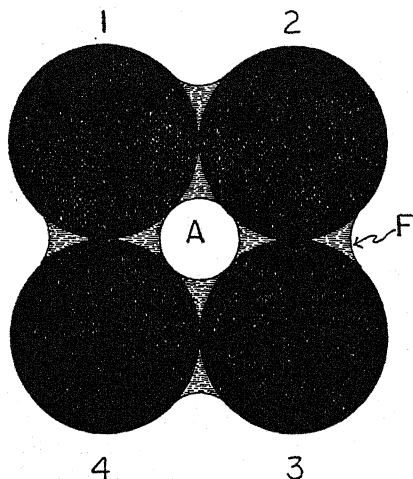


FIG. 3a

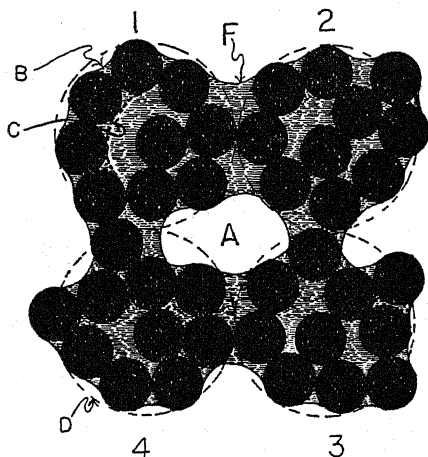


FIG 3b

FIG. 3. RETENTION OF MOISTURE IN A SAND AND IN A FRAGMENTED HEAVY SOIL
a (Left), postulated location at the moisture equivalent in pore space of sand: 1, 2, 3, 4, four grains; F , pendular water retained; A , unfilled pore space passing through the cell.

b (Right), postulated location at the moisture equivalent in pore space of porous aggregates: 1, 2, 3, 4, four fragments; dashed circles, D , of same radius as grains of *a*; F , retained water within the fragments; A , unfilled pore space, which usually will be obliterated by the centrifugal field. Microscopic hysteresis is illustrated by aggregate 1. Only the capillary curvatures, B , exist when emptying; the equal curvatures B and C exist when filling and much of the interior of the aggregate is unfilled.

The curvatures of the liquid surfaces are the same in *a* and *b*.

the density of water, then with M and P expressed as decimals rather than as percentages,

$$P = (M/d)/[(1/\rho) + M/d], \text{ or if } d = 1$$

$$P = M/[(1/\rho) + M] \quad (1)$$

The volume weight, v , of the dry soil, and the moisture equivalent M also may be used, under the conditions postulated, to calculate the porosity. The relation is, with $d = 1$

$$P = vM \quad (2)$$

These equations are justified by considerations on the distribution of water in the upper capillary range (approximately pF 2.6 to 3.3).³

³ In general, the water M , held in the upper capillary range, may be divided into three parts: a part, E_p , is in the pore space, that is, as liquid water; a part, E_o , is associated with organic matter; and finally, a part, E_m , is associated with the mineral component. The part E_m may exist as adsorbed water held by surface forces, or as water associated with a mineral lattice, such as would occur with montmorillonite, or both, or, finally as gel water such as that associated with iron and aluminum oxides. Hence,

Some conclusions concerning moisture equivalent

The detailed examination of the behavior of initially saturated nonporous and porous packings in a centrifugal field of 1000 gravity suggests the following conclusions when the soil does not swell appreciably [negligible swelling permits equation (3') to be used]:

$$M = E_p + E_o + E_m \quad (1')$$

The terms E_o and E_m do not include the pore water associated with their respective components.

As far as the upper capillary range is concerned, it appears sufficient to consider pore water and only those parts of E_o and E_m that are associated with swelling, and write equation (1) as

$$M = E_p + E_s \quad (2')$$

The single term E_s represents the part of $E_o + E_m$ associated with swelling. Surface-adsorbed water need not be considered. It is to be observed that, from a soil wetted to a point in the upper capillary range, the bulk of water recovered in processes used to determine the constants of this range is not that of constitution; water held by surface adsorption is negligible in soils of coarse texture; saturation prevails in those of fine textures; and finally, in soils of intermediate texture, saturation occurs at textures for which capillary water would still be large compared to that held by surface adsorption.

If E_o and E_m are small compared to E_p , that is to say, the soil contains little organic matter, and the water E_m associated with the minerals is inappreciable (E_s is negligible; that is, swelling is slight), then water held in the upper capillary range is chiefly within the pore space, and approximately,

$$M = E_p \quad (3')$$

The pore space may or may not be saturated.

If all pores are completely filled, the porosity, P , may easily be obtained. If ρ is the density of soil solids and d is the density of water, then, with M and P expressed as decimals rather than as percentages,

$$P = (M/d)/[(1/\rho) + M/d], \text{ or if } d = 1 \\ P = M/[(1/\rho) + M] \quad (4')$$

If the pores are not completely filled, the pore space P_w occupied by water is determinable. Let U be the void space, in unit mass of soil solids, that is unfilled. Then, setting as an approximation, $d = 1$, we easily find,

$$P_w = M/[(1/\rho) + M + U] \quad (5')$$

The total pore space $P = P_w + P_u$ where $P_u = U/[(1/\rho) + M + U]$. The fraction of the pore space saturated is P_w/P .

The volume weight, v , of the dry soil, and the water M also may be used, under the conditions postulated, to calculate the porosity. M is supposed to be expressed on a weight basis, that is, the weight of water per unit weight of dry soil. The relation, for a saturated pore space, is $P = vM/d$, or if $d = 1$

$$P = vM \quad (6')$$

By the use of the relation $P = (\rho - v)/\rho$, equation (6') is easily shown to be compatible with equation (4'). Equation (6') is probably restricted to rough work, since v , the volume weight, cannot be as accurately determined as ρ , the density of the solids.

If a soil has sufficiently fine texture, its textural pore space will remain filled with water when placed in the field; a critical texture should exist, and all soils finer than this should remain saturated, all coarser should not. The difference between the water actually present and that required for saturation is, in the case of unsaturated soils, variable and may be small or large, depending upon texture.

When a soil in the fragmented state is saturated and subjected to the field, the secondary pore space, if the fragments can be deformed by the field, will be largely eliminated, and the water held, after the field has been applied, will closely equal that which would remain under a similar field in the pore space of the unfragmented soil; for example, a clayey horizon.

In those cases where only textural pore space exists, and where the water held at moisture equivalent is that required just to saturate the pore space, as expressed by equations (1) and (2), then the porosity of many soils may, it appears, be computed approximately from textural data. An empirical relation such as Olmstead's (12), or Middleton's (8), will determine the moisture equivalent, and equation (1) or (2) will give the corresponding porosity.

It is not expected that the moisture equivalent will measure the porosities of A horizons of soils; e.g., the granular horizon of a chernozem.⁴

Compaction occurring in the outer boundary where the centrifugal field is greatest may prevent drainage and leave an excess of water close to or at this boundary, especially if the centrifugal field has been applied too rapidly.⁵ A gradient in compaction would probably give rise to a moisture gradient, a phenomenon which has been observed; at least, the moisture gradient has been observed to exist in a sample which has been subjected to a centrifugal field (19).

The differences between moisture equivalent determinations made by the centrifuge method and the suction method of Bouyoucos (2, 3) on identical soils become somewhat less puzzling. The data of Pinckney and Alway (13) show considerable disagreement with coarser textures but good agreement with heavier soils. This is to be expected, since neither the suction forces nor those arising from the centrifugal fields are adequate to empty the pores of single fragments in heavier soils but are capable of destroying the secondary pore space. With coarse textures such as sands, both methods produce drainage. The weaker force fields of the suction methods are incapable of emptying some of the finer pores enclosing pendular water, that are emptied by the stronger centrifugal fields; hence, more

⁴ When the soil contains much organic matter, equation (3') will not apply. No attempt is made, in this writing, to investigate the terms E_o and E_m , and further conclusions are not warranted on this point. Appreciable swelling will render the conclusions reached untenable and bar the application of equation (4'). The requirement for use of equation (4') is that the external dimensions of the sample remain essentially unaltered in the wet and dry states. Shrinkage fissures may develop, but these close on wetting and are included in the porosity determined in the dry state. Further investigation is required.

⁵ Samples are occasionally found among fine-textured soils in which, during moisture equivalent determinations, the water collects on top of the soil in the box, instead of being thrown out by the centrifugal field. By running the centrifuge very slowly for a sufficient time before bringing it up to full speed, this condition can be avoided. In other words, it is necessary to give the secondary pores, where they are extremely fine, time to drain before the field becomes strong enough to collapse them.

water remains in the sample. For reliable results with suction methods it appears essential to use a silt barrier to prevent air-cutting and its consequent reduction of the suction force; these methods have been discussed by Schofield (15), Schofield and Botellio da Costa (14), and Botellio da Costa and Alves (1).

Moisture equivalents of monolith samples

The foregoing conclusions should also apply to moisture equivalent determinations on monolith samples. For good agreement of observed and calculated values, correction must be made for nonporous stony material which has been partly discarded from the fragmented sample. The structural pore space is usually blocky [Nikiforoff's nomenclature (11)] in clayey horizons and is small compared to the textural. The contrast is even more pronounced after the field has acted upon it; the textural pore space will be saturated. The differences arising between the soil in the natural and in the fragmented condition will depend upon how completely the field has destroyed the secondary pore space of the latter. Less thorough destruction will mean larger differences.

Experimental investigations

To ascertain how far the conclusions reached in the foregoing discussion are warranted, moisture equivalents and porosities of three soils were measured by the ordinary centrifugal methods. These were various horizons of Miami silty clay loam, Miami silt loam, and Chester loam, soils that are fully described elsewhere (18). Moisture equivalents were determined on samples in monolith form (designated M_a); and on samples in fragmented form (M_g) as is usually done for moisture equivalent determinations. Porosities of the soils in their natural state were obtained from measurements of field volume-weights of the dry soil and densities of total solids. Porosities were also obtained for the fragmented state. Tables 1, 2, and 3 show the observed and calculated data for moisture equivalents and porosities. Mechanical analyses of these soils were also made and are shown in table 4.

The observed volume-weights and grain densities are shown in table 1. Table 1 also shows data⁶ on three samples—C1671, C1672, and C1673—of Chester loam taken from a location different from that of samples C6628, C6629, and C6630. These soils are described fully elsewhere (6). The volume-weights shown are field volume-weights taken when the soil was fairly dry but not in an air-dried condition.

Values of moisture equivalent measured both for fragmented and for monolith samples of the soils listed in table 1, are shown in table 2. Likewise, values calculated from porosities and grain densities, and also from textural data are given. The values for fragmented samples were measured by the usual procedure. Those for monolith samples were determined by an identical procedure. The block samples were carefully fitted to the boxes in every case. The values of M_a are shown both without correction and with correction for the stony material dis-

⁶ The data were taken entirely by Dr. L. B. Olmstead, who has kindly given his permission for their use here.

carded in the fragmented sample. The correction is made from the value W_s/W , where W_s is the weight of soil passing a 2-mm. sieve and W is the weight of the entire soil, including its stony content greater than 2 mm. Values of the moisture equivalent of the soils calculated from textural data by the normal relation of Olmstead (12), are shown in column 4. The textural data for samples C6615 to C6630 inclusive, are shown in table 4. For samples C1671 to C1673, mechanical

TABLE 1

Volume-weights and grain densities for various horizons of Miami silty clay loam, Miami silt loam, and Chester loam

LABORATORY NUMBER	SOIL TYPE	HORIZON	VOLUME WEIGHT (ρ)		GRAIN DENSITY (ρ)
			Fragmented	Natural	
			gm./cc.	gm./cc.	gm./cc.
C6615	Miami silty clay loam	A ₁	1.00	1.16	2.59
C6616		A ₃	1.45	1.84	2.71
C6617		B ₂	1.12	1.82	2.73
C6618		B ₃	1.37	1.83	2.74
C6619		C	1.37	1.80	2.76
C6620		V _B	1.22	1.73	2.74
C6621	Miami silt loam	A ₁	1.11	1.12	2.59
C6622		A ₂	1.24	1.47	2.67
C6623		A ₃	1.30	1.63	2.68
C6624		B ₂	1.24	1.73	2.72
C6625		B ₃	1.19	1.64	2.74
C6626		C	1.53	1.85	2.77
C6627		V _B	1.23	1.74	2.73
C6628	Chester loam	A	1.09	1.24	2.70
C6629		B	1.25	1.55	2.76
C6630		C	1.23	1.49	2.84
C1671	Chester loam	A		1.20*	2.73
C1672		B		1.46	2.78
C1673		C		1.45	2.80

* Data by L. B. Olmstead.

analyses are available elsewhere (6). To calculate moisture equivalents from porosities, and grain densities, equation (1) can be solved, thus

$$M = \frac{1}{\rho} \cdot \frac{P}{1 - P} \quad (3)$$

M and P are expressed as decimals. This equation has been used to calculate the values listed in column 5 of table 2. P is obtained from the volume-weight and grain densities shown in table 1. (The values of P used are shown in table 3, column 2.)

The moisture equivalents observed for monolith samples agree better with

values calculated from equation (3) than do those observed on fragmented samples. This is to be expected since fragmented samples contain a residual secondary pore space after centrifuging. Monolith samples likewise contain a residue of the structural pore space but it is extremely small in the B and C horizons, where agreement is shown, since the structural pore space in these horizons is small compared to the secondary pore space of the fragmented sample.

TABLE 2

Summary of observed and calculated moisture equivalents of soils in table 1

LABORATORY NUMBER	MOISTURE EQUIVALENT*			MOISTURE EQUIVALENT*	
	M_g fragmented	M_a monolith		Calculated from equation (3)	Calculated from textural data
		Not corrected	Corrected†		
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
C6615	26	24	25	32	21
C6616	19	16	17	17	20
C6617	22	19	21	18	23
C6618	24	17	18	18	25
C6619	23	20	21	20	25
C6620	23	20	22	21	24
C6621	29	21	22	51	24
C6622	24	19	19	31	21
C6623	23	18	20	24	21
C6624	25	19	20	21	25
C6625	27	20	24	24	25
C6626	17	16	20	18	17
C6627	25	20	21	21	25
C6628	29	44	20
C6629	30	29	21
C6630	26	33	13
C1671	26‡	47	..
C1672	28	32	..
C1673	23	33	..

* Grams of water/gram of dry soil (expressed as per cent).

† The correction is made from the value W_s/W , where W_s is the weight of soil passing a 2-mm. sieve and W is the weight of the entire soil, including its stony content greater than 2 mm.

‡ Data by L. B. Olmstead.

The lack of agreement for sample C-6626 probably rests on the fact that some of the hard material discarded during preparation is porous. The differences shown for the other samples are in many cases caused by remnants of the secondary pore space persisting after centrifuging. With most of the B and C horizons the differences are not of large order. Wider divergence is shown by the values for the A horizons. This is expected, since the samples from this horizon

contain organic matter and have granular structure. Part of the difference probably comes from water absorbed by organic matter, but the greater part arises from the fact that the secondary pore space does not disappear on centrifuging in these lighter horizons, but does lose some of its water.

On the other hand, as is to be expected, the values calculated from textural data agree better with values observed for fragmented samples. The agreement is generally very good, except for the Chester soil, which probably presents some anomalies not covered by the empirical relation.

TABLE 3

Summary of observed and calculated porosities of soils in table 1

LABORATORY NUMBER	OBSERVED POROSITY		CALCULATED POROSITY FROM EQUATION (1) BY USE OF	
	Fragmented	Natural	M_g	M_a (corrected)
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
C6615	61.4	55	40	39
C6616	46.5	32	34	32
C6617	59.0	33	38	37
C6618	50.0	33	40	33
C6619	50.2	35	39	37
C6620	55.5	37	39	38
C6621	57.2	57	43	36
C6622	53.6	45	39	34
C6623	51.5	39	38	35
C6624	54.4	36	40	35
C6625	56.6	40	43	40
C6626	44.8	33	32	36
C6627	55.0	36	41	37
C6628	59.6	54	44	..
C6629	54.7	44	45	..
C6630	56.7	48	43	..
C1671	56*	42	..
C1672	47	44	..
C1673	48	39	..

* Data by L. B. Olmstead.

Observed and calculated values of porosity are shown in table 3. Column 2 shows the observed porosities for fragmented samples before centrifugation. Column 3 lists observed porosities (calculated from the volume-weights and grain densities of table 1) for the natural soil. The last two columns show porosities calculated by equation (1), from the observed values of moisture equivalent and grain density shown in tables 1 and 2. Only the corrected value of the moisture equivalent has been used to calculate the porosity of the monolith samples.

The porosities of the fragmented samples differ greatly from the values observed on natural soils, except in the A_1 horizons where fragmentation has been

insufficient to destroy the granular structure of the natural soil. An estimate of the compaction produced by centrifugation can be made by comparing columns 2 and 4, which list the results on fragmented soils.

The differences shown in table 3 can be largely ascribed to the degree in which the secondary porosity P_I has disappeared after centrifugation. The magnitude of the secondary porosity remaining can be computed from the values of the total porosity P and of the textural porosity P_T . P_T must be obtained by calculation, however. The last column shows values of the textural porosity ($P_{T'}$) referred to the volume of the aggregates only. The relation required for calculating P_I is⁷

$$P_I = (P - P_{T'}) / (1 - P_{T'}) \quad (4)$$

The values of P_I for the natural soils, obtained from the values of $P_{T'}$ given in column 5 and the values of P given in column 3 are as follows: For the A_1 horizons of Miami silty clay loam (sample C6615) we find 26 per cent; for the A_1 horizon of Miami silt loam (sample C6621) we find 32 per cent; for the A_2 horizon (C6622) of the same soil the value is 16 per cent; for the other horizons the secondary porosity has mostly disappeared. The residual secondary porosity of a fragmented sample, after centrifuging, can be similarly calculated, and for the soils in table 1 varies from 3 to 10 per cent (the values of P used for these estimates are those for natural soils, given in column 4).

A graphical comparison of equation (3) with experimental data is given in figure 4. The curve A is, in each diagram, a plot of equation (3); the value of $\rho M = P/(1-P)$ is plotted as a function of P (P on logarithmic scale). The points are experimental values of ρM and P .

Figure 4 includes the data of Davis and Adams (7); results obtained by combining the data of Olmstead (12) with that of Middleton, Slater and Byers (9); and the data presented in this paper. The porosities of Greenville loamy sand and Greenville sandy loam were calculated from moisture equivalent data given by Davis and Adams (7) and compared with the corresponding porosities observed by them. Since these are sands, there is much wider divergence, except for the heavier horizons of Greenville sandy loam. Finally, Olmstead (12) reports moisture equivalents for certain soils whose field volume-weights and density of soil solids have been given by Middleton, Slater, and Byers (9); these are sufficient for the computation of values of ρM and P .

⁷ To derive this relation let V_I be the volume of the structural pores, V_S the volume of solids, and V_T the volume of the textural pores. Then $V = V_I + V_S + V_T$. The volume of the aggregates V_a is then $V_a = V_S + V_T$. The textural porosity $P_T = V_T/V$. If, however, $P_{T'} = V_T/(V_T + V_S)$ is measured by determining the ratios of the void space V_T to the total ($V_T + V_S$) occupied by the voids and their associated solids, correction is required. This, for example, would be done in a fragmented sample of heavy soil where the water required to saturate the single fragments is made by a moisture equivalent determination and the weight of dry soil is determined by weighing.

From the definition of porosity, $P_I = P - P_T$. Since $P_{T'}$ only has been measured, a transformation to a new expression involving only $P_{T'}$ is required. To do this, it is to be observed that $(P_{T'}/P_T) = V/(V_T + V_S)$ or $P_{T'}/P_T = 1/(P_T + P_S)$. Now $P_S = 1 - P$; replacing P_S by this value and solving, we find $P_T = [(1 - P)/(1 - P_{T'})]P_{T'}$. Hence, $P_I = (P - P_{T'})/(1 - P_{T'})$.

Figure 4-1 shows data for the A₃ and B horizons of the monolith samples (Miami silty clay loam and Miami silt loam). Figure 4-3 shows all data for B horizons of heavy soils in which swelling is not appreciable. Figure 4-2 shows the remaining data. All of the data in figure 4-2 lie above curve A. The straight line B has been drawn through the data but has no theoretical foundation as far as this investigation goes.

TABLE 4
Mechanical analyses of certain Miami and Chester soils

LABORATORY NUMBER	FINE GRAVEL 2-1 MM.	COARSE SAND 1-0.5 MM.	MEDIUM SAND 0.5-0.25 MM.	FINE SAND 0.25-0.1 MM.	VERY FINE SAND 0.1-0.05 MM.	SILT 0.05-0.002 MM.	CLAY 0.002-0 MM.	ORGANIC MATTER BY H ₂ O ₂	MINERAL MATTER DIS- SOLVED BY H ₂ O ₂	RELATIVE WEIGHT OF SOIL <2 MM. W _s /W
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	
<i>Miami silty clay loam</i>										
C6615	1.4	4.9	8.5	15.1	11.2	39.6	13.8	5.1	0.4	.968
C6616	1.4	4.1	6.5	15.0	10.7	38.7	22.5	0.9	0.2	.927
C6617	0.8	3.2	5.2	12.7	9.4	36.6	31.3	0.7	0.1	.896
C6618	1.1	2.6	3.7	10.5	8.6	36.7	36.4	0.3	0.1	.962
C6619	0.9	2.2	3.0	9.1	7.9	41.3	35.1	0.3	0.2	.936
C6620	1.1	2.9	4.2	10.5	10.0	36.0	34.2	0.6	0.1	.916
<i>Miami silt loam</i>										
C6621	0.7	3.4	5.0	11.4	6.7	50.3	16.5	5.5	0.5	.974
C6622	0.9	3.4	5.4	11.9	7.0	51.4	18.0	1.6	0.4	.990
C6623	1.0	3.3	5.3	11.0	7.3	50.7	20.4	0.8	0.2	.921
C6624	1.5	3.9	5.6	11.4	7.9	33.0	35.9	0.6	0.2	.932
C6625	3.0	5.1	6.0	13.2	8.6	25.1	38.2	0.6	0.2	.836
C6626	5.2	6.8	6.2	13.3	11.7	38.9	17.6	0.2	0.1	.802
C6627	2.1	4.7	6.3	13.0	8.0	27.7	37.2	0.8	0.2	.937
<i>Chester loam</i>										
C6628	0.6	2.5	5.6	14.2	8.6	47.8	19.9	0.6	0.2	.992
C6629	0.3	1.9	4.7	11.5	8.4	49.7	23.1	0.3	0.1	.978
C6630	1.8	5.2	5.2	17.0	21.4	41.4	8.0	0.0	0.0	.994

FIELD CAPACITY AND NORMAL MOISTURE CAPACITY

The foregoing discussion sheds some light on the relation of field capacity and moisture equivalent. With soils that swell but slightly, the problem is one of texture and of the relative magnitudes of the controlling fields. With coarser-textured soils such as sands, a force field of 1 gravity will not remove as much water as one of 1000 gravity; hence field capacity is, for these soils, greater than their moisture equivalent. With fine-textured soils such as clays, differences are small, since neither field is capable of removing water from the textural pore space. Such as do occur arise from alterations of the secondary pore space.

Field capacities may be slightly lower, because the undisturbed secondary pore space may permit drainage under a force field of 1 gravity, and when subjected to a field of 1000 gravity, it may be reduced to a size sufficiently small to prevent drainage, and hence retain water.

The water-retention capacities of soils could be compared at 1 gravity if it were not for the variable secondary pore space introduced by the fragmentation of a soil. A field of 1000 gravity applied to a wet soil is sufficient to destroy most of the pore space and restore the soil to a state near its original field condition [compare with the work of Briggs and McLane (5)]. Thus, if a column of fragmented

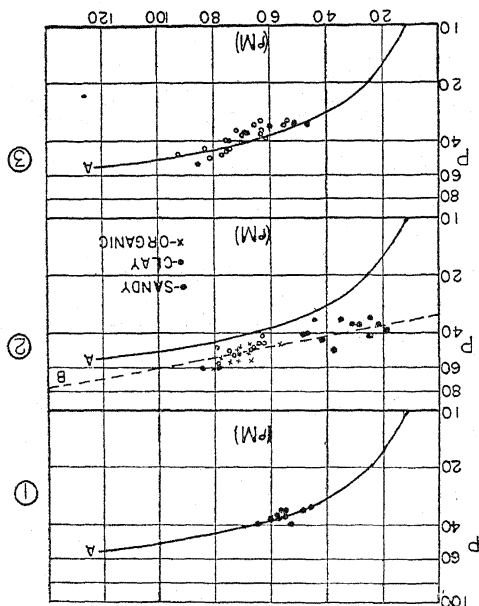


FIG. 4. THE QUANTITY $\rho M = \frac{P}{1-P}$ REPRESENTED AS A FUNCTION OF P
(P ON LOGARITHMIC SCALE)

1, monoliths; 2, soils that swell, and sands; 3, soils of small swelling. Curve A is the theoretical curve in each diagram; the points shown are experimental. Curve B of diagram 2 is drawn through the data but no analysis is given for it.

clay soil is allowed to drain at 1 gravity the water retained will be variable and amount to as much as twice the moisture equivalent. This represents storage of water by the secondary pore space, existing between the fragments. Caution must be taken when one attempts to attach significance to such phenomena, since no such pore space exists in the natural soil, and, at best, that existing in a fragmented soil is a somewhat variable quantity. Cultivation, for example, produces fragmentation which is only temporary.

On the other hand, retention measurements such as, for example, that called by Shaw "normal moisture capacity" (16) have value. The water absorbed lies almost completely within the fragments, with but little in the secondary pore

space unless the fragments are nonporous. In clay soils the moisture equivalent and normal moisture capacity should and do have almost identical values (12), since each substantially measures the saturation value of soil fragments.

SUMMARY

A discussion of soil moisture constants in the upper capillary range has been presented from the standpoint of soil physical conditions.

Some evidence has been presented which indicates that the water of a heavy soil, which does not swell appreciably, is, at moisture equivalent, largely contained in the textural pore space. At this moisture point the textural pore space is saturated, or nearly so. Conditions prevailing in a sand at moisture equivalent are quite different. The pore space is not usually saturated.

Formulas are given for calculating the porosity of a heavy soil when its moisture equivalent and volume-weight, or moisture equivalent and density of its solids, are known. The conclusions are based on limited data, and extensive study probably must be made to establish with certainty the behavior here postulated.

Just as soil physical conditions are important in transfer processes such as the passage of heat or water, so they must be considered when moisture constants of the upper capillary range, such as moisture equivalent, field capacity, and normal moisture capacity, are measured or used.

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INFLUENCE OF FERTILIZERS ON THE ACCUMULATION OF ROOTS FROM CLOSELY CLIPPED BENT GRASSES AND ON THE QUALITY OF THE TURF¹

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This experiment to determine the influence of various fertilizers on the accumulation of root materials under closely clipped bent grass and upon the quality of turf is a continuation of an experiment reported by DeFrance (2) in 1938, showing the results of 5 years of observation of the effect of different fertilizer ratios on Rhode Island (Colonial), creeping, and Piper velvet bent grasses. In general DeFrance's conclusions were that a fertilizer with a 10-6-4 ratio was the most satisfactory of those tested. Twenty per cent of nitrogen in the fertilizer gave the highest quality ratings for vigor, color, and density, but the turf became too spongy for practical putting green conditions. Fertilizer with 5 per cent nitrogen produced the finest textured grasses, but they were more susceptible to invasion by clover and weeds. Medium amounts of phosphorus tended to complement the beneficial effects of nitrogen, but larger amounts of phosphorus encouraged weeds. The addition of potassium appeared to have little effect upon the qualities estimated in the experiment, but encouraged the growth of clover.

Since these plots were in good condition and had been in operation since 1932² it was believed that an investigation of the accumulation of roots under these same treatments might lead to interesting findings. The effects of fertilizer treatments on the accumulation of grass roots under putting green conditions were previously considered by Evans (3) in England and by Sprague (7) of New Jersey. To obtain additional evidence concerning the effect of fertilizer treatment upon root accumulation, plugs of sod were removed periodically during 1939, 1940, and 1941, and estimates of root weights were made.

It must be made clear that the investigators were not measuring the effect of the various fertilizers on root growth, because the root mass of grasses consists of both living and dead roots. Sprague's (7) data gave evidence of this fact, since he found that soil treatments which produced an acid reaction in the soil, below pH 5.5, were associated with high root yields. Since the vigor of the tops was inversely correlated with root abundance, and many of the grass roots in the strongly acid soils appeared to be dead, the conclusion was drawn by Sprague that the roots produced in previous years had accumulated because the soil reaction was not favorable for their decay.

The active roots of bent grasses as well as of many other grasses are renewed annually. Stuckey (8) has recently reported evidence on the seasonal activity

¹ Contribution No. 638 of the Rhode Island Agricultural Experiment Station, Kingston, R. I.

² This work was initiated and was executed until 1936 by H. F. A. North.

of grass roots. Lyon and Buckman (4), summarizing the relationship between pH and the activity of bacteria and actinomycetes, write that below pH 5.5 these organisms are inactive, and slow decay is brought about by fungi. Since most bent grasses grow at pH ranges from 4.8 to 5.5, it is to be expected that decay will be slow, and large quantities of roots will accumulate. It should be clear then that by sampling a putting green sod one does not obtain a measure of either growth or decay but an indication of the state of equilibrium between these two opposite phenomena.

The fertilizer treatments used are designated as follows:

10- 6-4	Standard
5- 6-4	Low nitrogen
20- 6-4	High nitrogen
10-12-4	High phosphorus
10- 0-4	Low phosphorus
10- 6-8	High potassium
10- 6-0	Low potassium
10- 0-0	Low phosphorus and potassium

The grasses were randomized in triplicate blocks to overcome any heterogeneity of the soil, and each fertilizer treatment was triplicated on each species of grass. The grasses used were R. I. bent (*Agrostis tenuis*), Washington creeping bent (*A. palustris*), and Piper velvet bent (*A. canina*).

The fertilizer mixtures contained three carriers of nitrogen: 50 per cent was furnished by ammonium sulfate, 30 per cent by activated sludge, and 20 per cent by nitrate of soda. The phosphorus was obtained from superphosphate, and the potassium from muriate of potash. The seasonal rate of application approximated 1500 pounds of fertilizer per acre. Four applications were made the first week of each of the following months: April, 30 per cent of total; May, 20 per cent; July, 20 per cent; and September, 30 per cent. Compost was applied during the same periods on all the bent greens, but Washington creeping bent was also composted in June and August in order to keep the green firm. The plots were mowed three times a week during the growing season at a height of $\frac{1}{4}$ inch, and the clippings were removed. Further cultural details are given in the paper by DeFrance (2).

METHOD OF OBTAINING ROOT WEIGHTS

The following technique was used in obtaining the samples. A steel tube with an opening $\frac{7}{8}$ inch in diameter was inserted into the ground to a depth of 8 inches. During 1939 and 1940, three samples were removed from each plot at each sampling date. Since each treatment was in triplicate, nine samples altogether represented each fertilizer ratio at each sampling date for each species of bent grass. During 1941, five plugs were removed from each plot, making a total of 15 plugs from each treatment at each date of sampling. The top inch of each plug was cut off and discarded because of the great accumulation of stems and leaves near the surface. The use of compost several times a year for many years helps bury this part of the grass. Sprague (7) also discarded the tops of his sod plugs for similar reasons.

The plugs of sod were carefully separated from soil by placing them on a wire screen where they were washed with a gentle stream of water from a hose. After washing, the roots were rapidly dried at 70°C., then they were placed in porcelain crucibles and dried to constant weight at 100°C. Each crucible of roots was then ignited at dull-red heat until the organic material was completely ashed. The loss on ignition is used as a measure of the organic portion of the roots in each plug. Loss of weight on ignition is believed to be a more satisfactory method of estimating root weights than simply using dry weights, since the dry weight includes much very fine sand which clings to the roots.

The data showing weight of roots were obtained by changing the weight of loss on ignition to pounds per 1000 square feet of area. The results obtained each year for each species of bent grass were analyzed at each sampling period for significance by the analysis of variance technique. With Washington creeping bent the odds were nearly always 19:1 or better that a significant difference occurred in root weights as a result of different fertilizer ratios. Rhode Island bent and velvet bent approached this level of significance but seldom exceeded it. In order to minimize the effects of experimental error which were operating in the individual analyses, an average was obtained for each species of bent grass for each ratio over the 3-year period, 1939 to 1941. In each of these 3-year averages, 117 individual samples are included for each fertilizer ratio with each species of grass.

These averages are presented in table 1 along with data for the green weights of tops, average quality factors, pH values, and incidence of white clover. The figures representing weights of tops are expressed as grams of clippings produced per day. No complete clipping record was kept, but samples were taken at intervals during the experiment. The quality factors average was calculated by averaging the quality estimates for vigor, color, and density made during the years 1939, 1940, and 1941. This quality factor represents in general the visible influence of each ratio on the bent grasses. The relative amount of clover for each treatment is obtained from the 3 year average of the clover estimated to be present in the plots.

RESULTS AND DISCUSSION

The data in table 1 indicate that Piper velvet bent accumulated more roots than either Rhode Island bent or Washington creeping bent. The latter two grasses were similar in production of roots. It is interesting to note that velvet bent grass becomes "root bound," and increasing amounts of nitrogen failed to change significantly the weight of roots that accumulated. Why this happens is not known, but either velvet bent roots grow faster or they are more difficult to decompose than those of the other two grasses. High nitrogen increased to a highly significant degree the quantity of roots of Rhode Island bent. Washington creeping bent produced the smallest quantity of roots at the 5 per cent nitrogen level in the fertilizer and responded significantly to each increase in nitrogen. With each 5 per cent increase in nitrogen the acidity increased by 0.2 of a pH unit, and the yields of clippings and the quality of the turf increased sig-

nificantly. It was manifest in these experiments that increasing the nitrogen improved the quality of the turf and increased the rate of growth. The data substantiate these observations. A definite increase in acidity as shown by a decrease of 0.2 of a pH unit might inhibit to a certain extent the microorganisms responsible for the decomposition of dead roots. On the other hand, increasing the amount of nitrogen given to the Rhode Island bent grass or Washington creeping bent may have caused an increase in roots as well as tops, so that more

TABLE 1

Effect of various fertilizer ratios on the accumulation of roots, quality of turf, yield of tops, and pH of soil

FERTILIZER	ROOTS PER 1000 SQUARE FEET OF AREA			AVERAGE QUALITY FACTOR*	AVERAGE DAILY GROWTH OF TOPS†	1940 AVERAGE pH	RELATIVE AMOUNT OF WHITE CLOVER‡
	R. I. bent	Piper velvet bent	Washington creeping bent				
	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>		<i>gm.</i>		
10- 0-0	102	316	120	78	40.90	5.58	6
N							
5- 6-4	108	323	80	73	44.71	5.63	54
10- 6-4	114	323	113	84	50.64	5.42	15
20- 6-4	138	317	164	89	68.78	5.26	1
P							
10- 0-4	115	340	124	80	47.07	5.59	21
10- 6-4	114	323	113	84	50.64	5.42	15
10-12-4	101	318	104	84	51.67	5.60	26
K							
10- 6-0	103	291	104	81	45.40	5.45	4
10- 6-4	114	323	113	84	50.64	5.42	15
10- 6-8	114	330	120	84	48.56	5.42	20
Difference necessary for significance							
19:1	12.6	11	19.8	2.5	7.13		
99:1	17.5	15.4	27.5	3.5	9.92		

* Calculated by averaging quality estimates for vigor, color, and density during 1939, 1940, and 1941.

† Clippings produced.

‡ Obtained from 3-year average of clover estimated to be present in plots.

growth and slower decay complement each other in causing a significant increase in root accumulations.

The comparison of phosphorus treatments shows that for each species of grass a definite decrease in weight of accumulated roots took place with an increment of P_2O_5 from 0 to 6 per cent in the fertilizer and also from 6 to 12 per cent. The decrease in weight from that found for the 10-0-4 ratio to that reported for 10-12-4 is highly significant for each species of bent grass. The data do not justify definite conclusions, but the addition of phosphorus need not be regarded as reducing the growth of the grass roots, but rather by making conditions more favorable for the decay of dead roots. It is fairly well established that not pH alone

but also the calcium concentration may have a decided influence on micro-organic activity in soil. The pH data show no evidence that superphosphate has influenced the acidity significantly. The amount of calcium in a soil treated for several years with a 10-12-4 fertilizer formulated with ordinary superphosphate would be considerable, since 20 per cent superphosphate has a CaO content ranging from 27 to 30 per cent.

Analyses³ presented in table 2 show that even in the control plot there was a seemingly adequate amount of available phosphorus. These data, obtained in the fall of 1942, 10 years after the experiment was started, indicate the residual effects of the various fertilizers on available phosphorus. Though they were not obtained at the same time as the root samples, they throw some light on the amount of phosphorus that may have existed at the time the samples were taken. The Truog and Meyer (9, 10) method for determining the readily available frac-

TABLE 2
Available Phosphorus in grass plots at various depths
Results in pounds per acre

FERTILIZER	AVAILABLE PHOSPHORUS											
	Rhode Island bent			Piper velvet bent			Washington creeping bent			Average		
	1-3"	3-5"	5-7"	1-3"	3-5"	5-7"	1-3"	3-5"	5-7"	1-3"	3-5"	5-7"
10- 0-0	114	38	34	86	60	20	73	67	39	91	55	31
10- 0-4	116	36	26	131	51	21	102	50	38	116	46	28
10- 6-0	180	41	43	214	116	62	179	58	37	191	72	44
10- 6-4	221	44	27	234	134	58	207	73	38	221	84	41
10- 6-8	206	41	30	258	130	42	177	67	38	214	79	37
5- 6-4	242	46	42	214	92	26	242	68	32	233	69	33
20- 6-4	148	40	36	178	92	52	120	70	33	149	67	40
10-12-4	298	70	40	201	167	52	290	125	42	263	121	45
Average..	191	45	35	190	105	42	174	72	37	185	74	38

tion of phosphates was modified to prevent interference by the rather large quantities of lead arsenate that had been applied. The arsenic was reduced with sodium bisulfate as recommended by Zinzadze (11). The accuracy of the technique was verified by the analysis of synthetic solutions. Each sample tested was a composite of ten cores. The top inch of sod was discarded and the remainder of each core was cut in 2-inch sections. The sections were air-dried and passed through a 20-mesh sieve to remove gravel and coarse roots. A considerable portion of the recent applications undoubtedly were discarded in the top inch of sod.

These data give the impression that phosphorus, even in the low-phosphorus plots, was available in adequate amounts to promote the growth of bent grasses. Sommer (6) and others have found that 1 to 2 p.p.m. of phosphorus in nutrient solution may be adequate for the growth of plants. Truog (9) placed the tentative

³ These analyses were made by J. Rynasiewicz, of the department of agricultural chemistry.

limits for adequate phosphorus as 50-75 pounds per acre of the furrow slice. Morgan (5) has classified bent grasses and putting greens as low in phosphorus requirement. A clear-cut relationship between root accumulations and amount of available phosphorus is not apparent. Sprague (7) also found a lack of correlation between root growth of grasses and the phosphorus content of the soil. The soil from plots treated with a 20-6-4 fertilizer contained less available phosphorus than any of the others treated with fertilizer containing 6 per cent P_2O_5 . The increased growth of grass due to high nitrogen may have used up more of the available phosphate.

Applications of phosphates in the fertilizers affected primarily the 1- to 3-inch zone of soil. This is to be expected, since mineral phosphates are known to penetrate slowly into soils. Also, the phosphates which are absorbed and translocated from lower levels may be released by decay from plant residues on the surface, thus adding to the amount present near the surface. Evidence of this is found in the plots receiving no phosphate in the fertilizer.

It is interesting to note in table 2 that the average quantities of available phosphorus for all types of fertilizer treatments were similar in the 1- to 3-inch zone for each type of grass. The same holds true for the available phosphorus in the 5- to 7-inch level of soil. A wide difference, however, exists in the average amounts of P_2O_5 found in the 3- to 5-inch level under the three kinds of bent grasses. At this level, the average is only 45 pounds of P_2O_5 per acre under R. I. bent, whereas it is 105 pounds under Piper velvet, and 72 pounds under creeping bent. This suggests that the roots of R. I. bent are most effective in collecting phosphorus from this soil zone, creeping bent is intermediate, and Piper velvet least effective.

During the 3 years 1939, 1940, and 1941 a moderate amount of phosphorus had a significant effect on the quality of the turf when properly balanced with 10 per cent nitrogen. Where the 5-6-4 fertilizer was used, the poorest quality turf resulted. The Piper velvet bent plots are still in existence and the visible differences in quality between the 5-6-4 and the 10-6-4 is very evident, the 10-6-4 being better by far. This adds emphasis to the belief that, to grow good-quality turf, attention must be given to the ratio of nitrogen to phosphorus in the complete fertilizer. Two parts of nitrogen to one of phosphoric acid should give a good balance.

Adding 4 per cent potash (K_2O) in the fertilizer without any phosphate caused a significant increase in root weights for Rhode Island bent and velvet bent. Increasing the potash (K_2O) in fertilizer containing phosphorus from 0 to 4 per cent caused an increase in root accumulation. This increase is highly significant statistically only in the case of velvet bent. As no significant difference in pH existed between plots receiving 10-6-0, 10-6-4, and 10-6-8, it cannot be claimed that the differences in this case are due to differences in pH. It is possible, of course, that increasing the potassium had so favorable effect on root growth that growth outstripped decay. A moderate amount of potassium had a favorable influence on the quality of the turf, but did not significantly influence the daily production of clippings.

Sprague (7) in his paper points out that the vigor of the tops was inversely correlated with root abundance. With the creeping bents studied, he found that large quantities of roots accumulated where the pH value of the soil was 5.5 or lower and that low pH and large quantities of roots were associated with low-quality turf. The nitrogen series of this experiment shows a positive correlation between the quality of the turf and increasing nitrogen. In the case of Rhode Island bent grass and Washington creeping bent an increasing weight of roots is associated with improved quality of the turf. This seems contrary to the findings of Sprague. On the other hand, the results in the phosphorus series (10-0-4 to 10-6-4) show a slight increase in quality with decreasing weight of roots, which is similar to Sprague's findings. The results showing accumulation of roots in the potassium series are again in opposition to the results in the phosphate series, since an increase in root weights is accompanied by an improvement in the quality of the turf. Reference to Piper velvet in the nitrogen series shows no significant difference for root weights among the 5-6-4, 10-6-4 and 20-6-4 fertilizers, but the improvement in quality of the turf is correlated with increasing amounts of nitrogen to a highly significant degree. From these relationships it seems apparent that root accumulations cannot be used as a guide to quality of turf. It is possible to maintain a putting green of suitable quality despite root accumulation and soil acidities ranging in pH from 5.2 to 5.6 if the proper kind of fertilizer is applied in sufficient quantities throughout the growing season.

The data in table 1 indicate that the nitrogen balance and the available potassium are both factors that influence the growth of white clover in putting greens. Since white clover is considered undesirable in a putting green, its control by fertilization should save many hours of weeding. The highest incidence of clover occurred where the 5-6-4 fertilizer ratio was used. With a 10-6-4 fertilizer the amount of clover found was moderately small, and with a 20-6-4 fertilizer white clover could scarcely survive. Also, in the absence of potassium in the fertilizer white clover had little power to invade the putting green. The evidence that phosphorus has influenced the clover in this experiment is not great. On the average, more clover appeared in the low-phosphate plot than in the 10-6-4 plot, in spite of less available phosphate being shown for the 10-0-4 plots. Quite possibly satisfactory putting greens could be maintained by applying a complete commercial fertilizer (10-6-4) only once during the growing season. The other top-dressings could be made with a mixture of the three nitrogen carriers when required. This would promote the growth of a high-quality turf without the addition of enough potassium to encourage white clover. Bengtson and Davis (1) have reported that potash applied to moderately acid plots usually has been accompanied by a decided reduction in the control of white clover.

CONCLUSIONS

Increasing the amounts of nitrogen or potassium applied to bent grass putting greens may increase the weight of accumulating roots, whereas large amounts of phosphorus may reduce root accumulations. The state of equilibrium between the growth and decay of grass roots does not materially affect the quality of the

turf if adequate nitrogen, balanced with a moderate amount of phosphorus and a small amount of potassium, is applied at suitable intervals.

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THE NITROGEN AND MINERAL CONTENTS OF SUGAR BEET SECTIONS

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A knowledge of the nitrogen, phosphorus, calcium, and magnesium contents of sugar beets, crowns, and leaves is important for the following reasons: (a) High nitrogen and mineral contents of the beet are objectionable from the sugar manufacturers' standpoint; (b) the nitrogen and phosphorus contents of the leaves and other sections of the plants are measures of the quantities of these elements taken from the soil; (c) a knowledge of the nitrogen and mineral constituents of the sections of the plant is valuable in determining how beets should be topped; (d) the nitrogen and mineral contents of the crowns and leaves may provide a rough index of the nutritive or manurial value of these sections of the plant.

ANALYSIS OF SAMPLES¹

Total nitrogen, phosphorus, calcium, and magnesium were determined according to the official methods for plant analysis. Duplicate determinations were made on all samples, and the averages of closely agreeing determinations were used.

Average percentages of total nitrogen, calculated to dry basis, in leaves, crowns, and beets from sugar beet plants grown in 1939 under various fertilizer treatments are presented in table 1.

The percentages of nitrogen varied in the different sections of the plant. They were more than four times as high in the leaves as in the beets and varied from less than twice as high in crown section C₃ to more than twice as high in C₁, as in the beet proper.

The average percentages of nitrogen in the various sections of the plants manured and fertilized with ammonium sulfate were higher than those in the plants nonmanured and unfertilized with ammonium sulfate.

The pounds of nitrogen in the various sections of the plants grown under different fertilizer treatments have been calculated from the actual yields per acre and the percentages of nitrogen found by analysis. The results are given in table 2.

The total nitrogen in the leaves of plants grown on the ammonium sulfate and manured plots was invariably higher than it was in the beets proper.

Should one purchase a nitrogen fertilizer, paying \$0.15 a pound for the nitrogen, the equivalent of that found in the beet tops and crowns taken from 1 acre of the manured or ammonium-sulfate-fertilized soil, the cost would be \$9.69. The nitrogen from the unfertilized acre would cost \$4.14. This has been removed from the soil by the beets, thus leaving the soil poorer to this degree. If the

¹ The nature of the field on which the beets were grown and the methods of sampling are given in a previous paper (1).

leaves and crowns were plowed under, they would be decomposed by bacteria and made available for future crops. If the crowns and leaves were fed and all the solid and liquid manure returned, the soil would have repossession of approx-

TABLE 1

Percentages of nitrogen in leaves, crowns, and beets, calculated to dry basis, product in 1939 with various fertilizers

PLOT	TREATMENT	NITROGEN				
		Leaves	Crown Section			Beets
			C ₁	C ₂	C ₃	
29	Check V ₂	2.38	1.34	1.19	1.00	0.57
36	Check V ₁	1.80	1.21	1.07	0.86	0.53
37	Manure	2.30	1.41	1.22	1.05	0.59
38	Manure, phosphorus, sulfur	2.76	1.43	1.33	1.11	0.65
39	Gypsum	2.22	1.14	0.99	0.83	0.54
40	Nitrogen	2.37	1.30	1.14	0.92	0.54
41	Phosphorus	1.87	1.08	0.98	0.84	0.40
42	Potassium	2.05	1.03	0.91	0.78	0.45
Average of nitrogen- and manure-fertilized.....		2.48	1.38	1.23	1.03	0.59
Average of non-nitrogen-fertilized.....		2.06	1.16	1.03	0.86	0.50

TABLE 2

Total nitrogen in leaves, crowns, and beets of plants grown with various fertilizers
Nitrogen in pounds per acre yield calculated to dry basis

PLOT	TREATMENT	NITROGEN				
		Leaves	Crown section			Beets
			C ₁	C ₂	C ₃	
29	Check V ₂	17.00	1.42	1.86	1.83	29.6
36	Check V ₁	16.97	0.93	1.40	1.39	25.5
37	Manure	57.90	2.39	3.25	3.47	49.9
38	Manure, phosphorus, sulfur	75.34	2.93	4.15	5.12	53.7
39	Gypsum	25.24	0.97	1.23	1.34	24.0
40	Nitrogen	35.05	1.15	1.42	1.73	25.0
41	Phosphorus	23.07	0.91	1.42	1.78	33.2
42	Potassium	34.62	1.15	1.51	1.84	23.7
Average of nitrogen- and manure-fertilized.....		56.09	2.16	2.94	3.44	42.87
Average of nonnitrogen-fertilized.....		23.38	1.08	1.48	1.64	27.20

imately three fifths of the nitrogen and one half of the phosphorus. Hence, the crowns and leaves have cost the producer from \$4.14 to \$9.69 per acre in soil nitrogen and thus should be worth approximately that much to him.

The average amount of nitrogen in beets, crowns, and leaves produced on 1 acre with manure or ammonium sulfate was 108 pounds, 39.7 per cent of which

was in the beet. The average pounds of nitrogen removed in the complete crop, from the nonnitrogen- and nonmanure-fertilized plots was 54.8 pounds, 50 per cent of which was in the beets. Therefore, ammonium sulfate and manure fertilizers tend to increase the nitrogen in the leaves to a greater extent than they do in the beet proper. Hence the protein nutritive value of leaves of beets grown with these fertilizers should be superior to that of beet leaves produced without fertilizers.

The percentages of phosphorus were greatest in the leaves and least in the beets. The percentages in the crowns decreased as the distance from the leaves increased. With the exceptions of the leaves the average percentages of phosphorus in the comparable sections of the manured and phosphorus-fertilized

TABLE 3

Average percentages of phosphorus in leaves, crowns, and beets, calculated to dry basis, produced on one acre with various fertilizers

PLOT	TREATMENT	PHOSPHORUS				
		Leaves	Crown Section			Beets
			C ₁	C ₂	C ₃	
29	Check V ₂	0.090	0.083	0.066	0.054	0.035
36	Check V ₁	0.087	0.090	0.078	0.058	0.041
37	Manure	0.119	0.169	0.149	0.127	0.092
38	Manure, phosphorus, sulfur	0.167	0.189	0.170	0.150	0.105
39	Gypsum	0.125	0.087	0.073	0.060	0.048
40	Nitrogen	0.126	0.093	0.078	0.066	0.043
41	Phosphorus	0.182	0.188	0.152	0.143	0.098
42	Potassium	0.173	0.126	0.116	0.101	0.074
Average of phosphorus- and manure-fertilized.....		0.156	0.182	0.157	0.140	0.098
Average of nonphosphorus- and non-manure-fertilized.....		0.120	0.096	0.082	0.068	0.048
Average of all.....		0.134	0.128	0.110	0.095	0.067

beets were approximately twice as great as in the sections of the nonmanured or nonphosphorus-fertilized beets.

The beets grown on the manured soil were as rich in phosphorus as were those receiving a liberal supply of soluble phosphorus.

The potassium fertilizer increased the percentages of phosphorus of the beets over that found in the check plots.

The ammonium sulfate fertilizers caused an increased concentration of nitrogen in the leaves whereas the phosphorus fertilizers caused an increased concentration of phosphorus in the beets proper.

If one were to purchase, at \$0.12 a pound, the equivalent of the phosphorus in the manured and phosphorus-fertilized crop of leaves, crowns, and beets grown on 1 acre, it would cost \$1.56. Approximately 37 per cent of the phosphorus is in crowns and leaves. The phosphorus in the crop of leaves, crowns, and beets produced on 1 acre without phosphorus or manure fertilizer would cost \$0.51.

Hence, though the cost of commercial nitrogen for the production of sugar beets may be prohibitive, the cost of the phosphorus is not. The value of the phosphorus in the beet tops and crowns produced on 1 acre with the phosphorus fertilizer should be worth \$0.58, as a fertilizer or a feed, whereas these products from the nonphosphorus-fertilized beets should be worth only \$0.25. These figures

TABLE 4

Average phosphorus content of leaves, crowns, and beets, of plants grown with various fertilizers
Phosphorus in pounds per acre yield, calculated to dry basis

PLOT	TREATMENT	PHOSPHORUS				
		Leaves	Crown Section			Beets
			C ₁	C ₂	C ₃	
29	Check V ₂	0.72	0.088	0.102	0.097	1.79
36	Check V ₁	0.82	0.069	0.098	0.094	1.95
37	Manure	2.98	0.24	0.39	0.43	7.74
38	Manure, phosphorus, sulfur	5.89	0.37	0.53	0.68	8.63
39	Gypsum	1.39	0.073	0.090	0.096	2.10
40	Nitrogen	1.87	0.083	0.097	0.124	2.03
41	Phosphorus	2.24	0.22	0.21	0.30	8.13
42	Potassium	2.93	0.14	0.19	0.24	3.91
Average of phosphorus- and manure-fertilized.....		3.70	0.28	0.38	0.47	8.17
Average of nonphosphorus- and non-manure-fertilized.....		1.55	0.09	0.12	0.13	2.36
Average of all.....		2.36	0.16	0.21	0.26	4.54

TABLE 5

Distribution of the phosphorus in leaves, crowns, and beets produced on 1 acre

	PHOSPHORUS-FERTILIZED	NONPHOSPHORUS-FERTILIZED
	<i>per cent</i>	<i>per cent</i>
Total pounds phosphorus.....	13.08	4.25
Percentage of total in beet.....	62.85	55.53
Percentage of total in crown section C ₁	2.15	2.12
Percentage of total in crown section C ₂	2.92	2.82
Percentage of total in crown section C ₃	3.63	3.06
Percentage of total in leaves.....	28.46	36.47

represent the amount the producer has depleted his soil of phosphorus in the production of the leaves and crowns.

The phosphorus- and manure-fertilized beet crop has removed from 1 acre annually 13 pounds of phosphorus, and the nonphosphorus- nonmanure-fertilized beet crop has removed only slightly over 4 pounds of phosphorus. The distribution of this phosphorus in the various sections of the beets was very different, however, as is evident from table 5.

The phosphorus fertilizers increased the proportion of total phosphorus in the beets and decreased the proportion in the leaves.

In tables 6 and 7 are given the weights of crown sections C_2 and C_3 , together with the weight and value of the nitrogen and phosphorus in the two crown sections based on actual yields. All results are given on the moist basis. The prices of fifteen cents a pound for the nitrogen and twelve cents a pound for phosphorus are values chosen for comparison and are based on an assumption

TABLE 6

Nitrogen and phosphorus of crown section C_2 and the value of nitrogen and phosphorus removed from 1 acre, reported on moist basis

PLOT	TREATMENT	ACTUAL YIELD OF C_2	N CONTENT OF C_2	VALUE OF N IN C_2 AT 15¢ A POUND	P CONTENT OF C_2	VALUE OF P IN C_2 AT 12¢ A POUND
		<i>pounds</i>	<i>pounds</i>		<i>pounds</i>	
29	Check V_2	318	0.82	\$0.12	0.04	\$0.005
36	Check V_1	310	0.70	0.11	0.05	0.005
37	Manure	978	2.30	0.34	0.27	0.040
38	Manure, phosphorus, sulfur	1136	3.23	0.48	0.44	0.050
39	Gypsum	242	0.54	0.08	0.04	0.005
40	Nitrogen	425	0.95	0.14	0.07	0.008
41	Phosphorus	265	0.63	0.09	0.09	0.010
42	Potassium	633	1.36	0.20	0.17	0.020

TABLE 7

Nitrogen and phosphorus of crown section C_3 and the value of nitrogen and phosphorus removed from 1 acre, reported on moist basis

PLOT	TREATMENT	ACTUAL YIELD OF C_3	N CONTENT OF C_3	VALUE OF N IN C_3 AT 15¢ A POUND	P CONTENT OF C_3	VALUE OF P IN C_3 AT 12¢ A POUND
		<i>pounds</i>	<i>pounds</i>		<i>pounds</i>	
29	Check V_2	403	0.82	\$0.12	0.05	\$0.006
36	Check V_1	409	0.71	0.12	0.05	0.006
37	Manure	1220	2.46	0.37	0.30	0.040
38	Manure, phosphorus, sulfur	1125	2.78	0.42	0.39	0.050
39	Gypsum	305	0.59	0.09	0.04	0.005
40	Nitrogen	585	1.17	0.17	0.09	0.012
41	Phosphorus	393	0.79	0.12	0.13	0.016
42	Potassium	849	1.65	0.25	0.21	0.025

that the nitrogen and phosphorus will become available to future plants. This assumption is in keeping with the work of Woodman and Bee (5) who after a study of the manurial value of beet tops conclude, "If the tops are plowed into the land it may be assumed that the whole of the nitrogen, phosphate, and potash is available as manure. Where stocks are allowed to consume them off the land, then it is assumed that only half the nitrogen goes into the excreta and three quarters each of phosphate and potash."

The weight of the crown C_2 from 1 acre of the plot fertilized with manure, phosphorus, and sulfur was 1,136 pounds, whereas that from the gypsum-fertilized soil was 242, the other plots falling between these limits. The weight of the crown C_3 produced on 1 acre of the manured soil was 1,220 pounds, whereas the averages of all the other plots were considerably less. The weight of the nitrogen in no case exceeded 3.23 pounds. This, if purchased at 15 cents a pound, would have cost 48 cents. The phosphorus in no case would have exceeded 0.44 pound, which at 12 cents a pound would cost 5 cents. It is evident that, judged from their nitrogen and phosphorus contents, the crowns have small manurial value, but because of their high sugar content they may have considerable value as stock food.

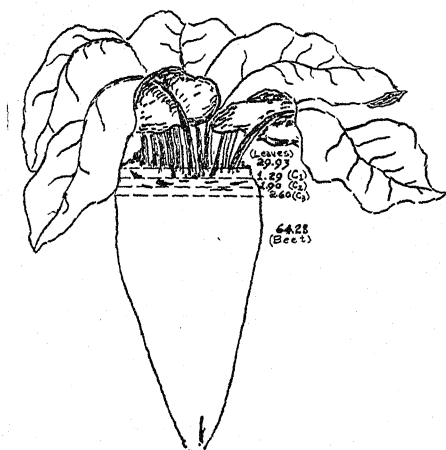


FIG. 1

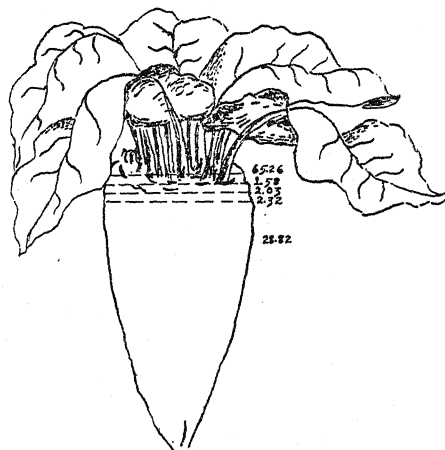


FIG. 2

FIG. 1. PERCENTAGE DISTRIBUTION OF TOTAL MOIST WEIGHT OF SUGAR BEET PLANT IN LEAVES, CROWNS, AND BEET

FIG. 2. PERCENTAGE DISTRIBUTION OF TOTAL NITROGEN OF SUGAR BEET PLANT IN LEAVES, CROWNS, AND BEET

The percentage distribution of the moist weight of the sugar beet plant, of nitrogen, and of phosphorus in the leaves, crowns, and beet is presented in figures 1, 2, and 3. Each result is the average of approximately 500 beets grown with and without fertilizers.

The beet leaves contained 29.93 per cent of the total moist weight, 65.26 per cent of the total nitrogen, and 49.67 per cent of the total phosphorus. More than half of the phosphorus and nitrogen removed in the beet crop is found in the tops and crowns and could be returned to the soil.

The calcium content of the various sections of the sugar beet plant varied widely, as shown in table 8. It was highest in the leaves and lowest in the beet and the crowns carried intermediate concentrations. The data suggest that the fertilizers decreased the calcium content of the crowns and leaves.

As was the case with nitrogen, phosphorus, and calcium, the greatest concen-

tration of the magnesium was in the leaves, and the smallest in the beet proper, with intermediate concentrations in the crowns.

The composition of leaves, crown sections, and beets of plants grown with and without manure, and the average composition of 14 crops of first, second, and third crop alfalfa grown on this same soil are given in table 10.

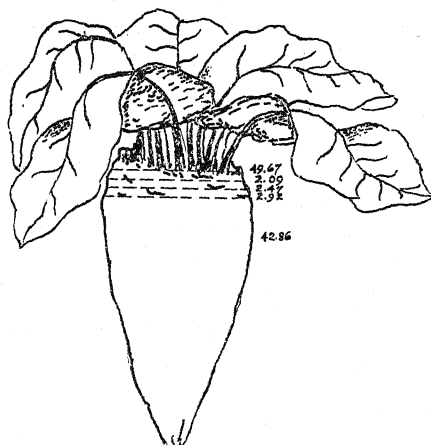


FIG. 3. PERCENTAGE DISTRIBUTION OF TOTAL PHOSPHORUS OF SUGAR BEET PLANT IN LEAVES, CROWNS, AND BEET

TABLE 8

Percentages of calcium in leaves, crowns, and beets, calculated to dry basis, produced with various fertilizers

PLOT	TREATMENT	CALCIUM				
		Leaves	Crown Section			Beets
			C ₁	C ₂	C ₃	
29	Check V ₂	3.12	1.52	1.30	0.82	0.26
36	Check V ₁	3.11	1.48	1.31	0.82	0.25
37	Manure	1.55	0.88	0.63	0.44	0.20
38	Manure, phosphorus, sulfur	1.56	0.89	0.74	0.48	0.22
39	Gypsum	2.62	1.66	1.43	0.97	0.32
40	Nitrogen	2.32	1.54	1.28	0.84	0.29
41	Phosphorus	1.46	1.17	0.73	0.53	0.22
42	Potassium	1.58	1.06	0.88	0.55	0.22
Average unfertilized		3.12	1.50	1.31	0.82	0.26
Average fertilized		1.85	1.20	0.95	0.64	0.25

Two facts must be borne in mind when interpreting the results given in table 10: first, the results are reported on the dry basis; and second, the chemical analyses represent the percentages of the different elements in the products. Approximately 6 tons of green leaves would be needed to yield 1 ton of dry leaves, and approximately 1.2 tons of properly cured alfalfa or 5 to 6 tons of green al-

falfa, to yield 1 ton of dry alfalfa. From the chemical analyses one cannot judge the coefficient of digestibility of the product or the biological value of the protein. These last two factors can be determined only by feeding the product. The analyses indicate, however, that better results would be obtained when phosphorus supplements (5) were fed with the leaves and crowns than when phosphorus supplements were not fed. Some workers recommend the addition of calcium salts to the ration so as to neutralize any oxalic acid that may be present.

TABLE 9

Percentages of magnesium in leaves, crowns, and beets, calculated to dry basis, produced with various fertilizers

PLOT	TREATMENT	MAGNESIUM				
		Leaves	Crown Section			Beets
			C ₁	C ₂	C ₃	
29	Check V ₂	1.74	0.61	0.59	0.42	0.31
36	Check V ₁	1.55	0.68	0.50	0.34	0.29
37	Manure	1.08	0.60	0.47	0.37	0.28
38	Manure, phosphorus, sulfur	1.05	0.61	0.50	0.36	0.26
39	Gypsum	1.35	0.69	0.53	0.40	0.31
40	Nitrogen	1.35	0.69	0.59	0.41	0.33
41	Phosphorus	1.07	1.12	0.54	0.41	0.26
42	Potassium	1.05	0.79	0.57	0.38	0.27
Average unfertilized		1.65	0.65	0.55	0.38	0.30
Average fertilized		1.16	0.75	0.53	0.39	0.29

TABLE 10

Percentages of nitrogen, phosphorus, calcium, and magnesium in leaves and crowns of sugar beets, and in alfalfa, calculated to dry basis

PRODUCT	NITROGEN	PHOSPHORUS	CALCIUM	MAGNESIUM
Beet leaves produced with manure.....	2.30	0.119	1.55	1.08
Beet leaves produced without manure....	2.09	0.089	3.12	1.65
Beet crowns, produced with manure.....	1.41	0.169	0.88	0.60
Beet crowns produced without manure....	1.28	0.091	1.50	0.65
First crop alfalfa.....	2.89	0.244	0.19	0.34
Second crop alfalfa.....	3.00	0.251	0.18	0.35
Third crop alfalfa.....	3.34	0.273	0.20	0.38

The limited analytical work done on these beets by us indicates the oxalic acid content to be extremely low.

Woodman and Bee (6) in six tests with sheep, each extending over a 22-day period, found the digestive coefficient of the various beet constituents to be: organic matter 78.5, crude protein 70.2, ether extract 62.8, N-free extractives 82.6, crude fiber 71.1. Hence, the digestibility of beet leaves and crowns compares favorably with that of alfalfa hay.

According to Maynard and co-workers (4) 1.4 tons of tops and crowns of beets when fed to lambs in dry lots with grain and alfalfa will replace about 20 pounds of shelled corn and 100 pounds of alfalfa. Therefore 6 tons of green leaves and crowns, which is approximately the equivalent of 1 ton of the dry material, should be the equivalent of 86 pounds of corn and 430 pounds of alfalfa hay.

Holden (2) found, as an average of six feeding tests, that the tops from 16 tons of sugar beets have the same feeding value as 1 ton of alfalfa hay and 491 pounds of corn. In a later work he (3) found no great difference in the value of corn silage, beet top silage, beet tops, and cull potatoes when fed with a ration of corn, cotton seed cake, and alfalfa. Ensiling beet tops increased their feeding value, but it was doubtful whether the increase was sufficient to pay for the ensiling.

SUMMARY

Sugar beet plants were grown on a highly calcareous soil with and without fertilizer. They were separated into the beet proper, crowns, and leaves and analyzed for nitrogen, phosphorus, calcium, and magnesium. The percentages of nitrogen were greatest in the leaves and lowest in the beets. In the crown sections, the percentages were greater the nearer the section was to the leaves.

The average number of pounds of nitrogen in the tops and crowns of the beets produced on 1 acre with manure or ammonium sulfate was 64.6. This nitrogen, at \$0.15 a pound, would cost \$9.69. These values represent the extent to which the soil had been depleted of its nitrogen by the crowns and tops and could not be considered a profit to the producer. The average number of pounds of nitrogen in the tops and crowns on the nonmanured plots unfertilized with ammonium sulfate was 27.6, which would have cost the farmer in reduced soil fertility \$4.14.

The phosphorus content of all sections of the sugar beet plant was increased by manure and phosphorus fertilizer. The percentages of phosphorus were considerably lower in the beets than in the leaves. The average number of pounds of phosphorus in the leaves and tops of beets produced on 1 acre with manure and phosphorus fertilizer was 4.8. The phosphorus in the same sections of the nonmanured, nonphosphorus-fertilized beets was 1.9 pounds. The cost of either as commercial fertilizers would be small.

The percentages of calcium and magnesium were greatest in the leaves and least in the beets. The quantity in the crowns was greatest next to the leaves and decreased as the distance from the leaves increased.

The beet leaves contained approximately 30 per cent of the total moist weight, 65 per cent of the total nitrogen, and 50 per cent of the total phosphorus.

The nitrogen content of crowns and leaves computed to the dry basis approximates that of first crop alfalfa. Feeding tests made by Woodman and Bee indicate that the coefficient of digestibility compares favorably with that of alfalfa. Feeding tests by Maynard and coworkers prove that 1 ton of moist beet tops and crowns approximate 14 pounds of shelled corn and 72 pounds of alfalfa in feeding value. The phosphorus content of the leaves and crowns of sugar beets is lower than that of alfalfa, and it seems highly probable that their nutritive value would be increased by a phosphorus supplement.

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PREVENTION OF CALCIUM CARBONATE PRECIPITATION IN SOIL SOLUTIONS AND WATERS BY SODIUM HEXAMETAPHOSPHATE¹

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Precipitation of calcium carbonate often occurs in extracted soil solutions containing appreciable concentrations of calcium and bicarbonate ions. Similar changes in composition occur in natural and synthetic waters during storage for long-time soil experiments. This results from a loss of carbon dioxide to the atmosphere, which occurs even in closed containers. Acidification of soil solutions and extracts at the time of analysis restores the calcium to solution, but this precludes the determination of carbonate and bicarbonate and the anion of the added acid.

Glassy sodium hexametaphosphate at the low concentrations of 1 to 5 p.p.m. has been used successfully in recent years in the stabilization of irrigation waters containing anhydrous ammonia as fertilizer (1, 8, 12), of industrial and municipal water supplies (13), and of brines (7). The fundamental mechanism of this "threshold treatment" has not yet been completely established (1, 5, 8). It interferes with the formation of calcium carbonate crystals and does not appear to prevent the conversion of bicarbonate to carbonate. The metaphosphate does not interfere with the determination of the quantities of calcium, carbonate, and bicarbonate ions usually encountered. This application of hexametaphosphate is an outgrowth of its prior use in stoichiometric concentrations to soften hard waters by virtue of its ability to "sequester" calcium into stable soluble calcium complexes (4).

The adaptation of the threshold treatment to soil solutions and waters to prevent deposition of calcium carbonate on standing was the object of the present investigation. In the case of waters used in percolation and leaching experiments on soils, it is important to demonstrate that such treatment has no effect, *per se*, on the soil. Permeability and exchangeable base studies have been made to examine this possibility.

EXPERIMENTAL METHODS AND RESULTS

The glassy sodium hexametaphosphate, $(\text{NaPO}_3)_6$, used in this investigation was prepared by heating sodium dihydrogen orthophosphate in a platinum dish for 2 hours in a muffle furnace at 1000°C. The melt was cooled rapidly by immersion of the lower part of the dish in water while covered by a watchglass to

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prevent losses on solidification. Although the constitution of the polymer thus formed is in question, it is commonly referred to as a hexametaphosphate.

Effectiveness of stabilization

The ability of sodium hexametaphosphate to stabilize soil solutions is exemplified by results obtained with a soil solution extracted from a sample of *Hesperia* sandy loam containing 10.4 per cent moisture. This solution was obtained by the pressure-membrane method (10, 11). The concentrations of calcium, carbonate, and bicarbonate ions increased during the extraction as a result of a progressive increase in carbon dioxide pressure in the extraction chamber caused by microbiological respiration. This effect has been discussed more fully elsewhere (10).

The solution (total volume 104 ml.) was removed in seven fractions, varying from 9 to 20 ml. The extraction occupied the period from September 16 to 19,

TABLE 1
Stabilization of a soil solution from Hesperia sandy loam by 2 p.p.m. sodium hexametaphosphate

FRACTION NUMBER	Ca ⁺⁺			CO ₃ ⁻⁻			HCO ₃ ⁻			pH		
	9-20-42 initial	10-27-42 treated	10-27-42 un- treated	9-20-42 initial	10-27-42 treated	10-27-42 un- treated	9-20-42 initial	10-27-42 treated	10-27-42 un- treated	9-20-42 initial	10-27-42 treated	10-27-42 un- treated
	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.	m.e./l.			
1	13.7	14.0	14.0	0.01	0.01	0.01	1.10	1.20	1.20	7.7	7.7	7.7
2	15.7	15.6	15.6	0.01	0.01	0.01	1.20	1.20	1.20	7.6	7.6	7.5
3	17.2	17.1	17.7	0.05	0.05	0.04	2.15	2.35	2.36	8.3	8.3	8.2
4	18.3	18.5	16.4	0.11	0.14	0.03	3.69	3.86	1.37	8.4	8.5	8.2
5	19.5	19.0	15.9	0.14	0.18	0.03	4.76	4.82	1.77	8.4	8.5	8.1
6	20.2	20.0	15.8	0.15	0.21	0.02	5.39	5.69	1.38	8.4	8.5	8.0
7		21.0	16.7	0.22	0.36	0.01	6.28	6.34	1.29	8.5	8.7	7.9

1942. As each fraction was removed, a portion of it was treated with a solution containing 1000 p.p.m. of sodium metaphosphate to provide a final concentration of 2 p.p.m. On September 20, the seven untreated fractions were analyzed by semimicroanalytical methods (9) except for sodium, which was determined by a gravimetric uranyl zinc acetate procedure (16). The carbonate and bicarbonate values were calculated by means of the carbonate equilibria slide rule of Hirsch (6) from pH values and total alkalinity to methyl orange. The remainder of the untreated portions and the treated samples were set aside in small stoppered glass bottles and analyzed 37 days later.

The results for calcium, carbonate, and bicarbonate ions and pH values are reported in table 1. Minor variations can be ascribed to analytical errors. The average concentrations of other ions, in milliequivalents per liter, are as follows: Mg, 5; K, 2; SO₄, 3; Cl, 3; NO₃, 17. After 37 days, the untreated portions of fractions 1 to 3 inclusive retained their initial composition. The untreated portions of the more concentrated fractions, 4 to 7 inclusive, lost calcium carbonate by

precipitation. Equilibrium values were approximately as follows: Ca, 16; CO_3 , 0.02; HCO_3 , 1.4; pH, 8.0. The treated portions of these fractions, however, retained their initial contents of calcium and bicarbonate, and the carbonate concentrations and pH values increased somewhat. The latter effect indicates that the metaphosphate does not inhibit the conversion of bicarbonate to carbonate; stated otherwise, loss of carbon dioxide from the solutions was not prevented. Although the absolute increase in carbonate may appear slight, it is nonetheless real. When these values are calculated by the usual phenolphthalein-methyl-orange titration procedure the effect is even more pronounced. The magnesium concentration did not decrease on standing.

The stabilization of these samples indicates that the calcium content and the alkalinity of similar solutions can be maintained during storage for weeks by the addition of 2 p.p.m. of sodium hexametaphosphate. Moreover, the calcium-carbonate-bicarbonate systems of the solutions of table 1 represent a higher level of instability than is usually encountered in soil solutions and waters.

Effect of metaphosphate on soil permeability

A sample of Fallbrook loam, a nonsaline slightly calcareous soil virtually free of soluble and exchangeable sodium was used for this study. The synthetic stock water contained 8.4 m.e. of calcium chloride and 5.6 m.e. of sodium chloride per liter. The chlorides were used in order to ensure constancy of composition throughout the experiment. The results obtained are applicable to waters containing bicarbonate, because both soil permeability and the action of the metaphosphate are related primarily to the cation.

Sodium hexametaphosphate was added to the synthetic water in the following concentrations: 1, 2, 4, 10, and 100 p.p.m. All five waters became turbid, but the waters containing 1 and 2 p.p.m. only very slightly so. After filtration of samples of the five waters through unglazed ceramic crucibles and hydration of the metaphosphate to orthophosphate in boiling acid solution, photometric determination showed the filtrates to contain the following concentrations of $(\text{NaPO}_3)_6$, respectively: 0.07, 0.8, 1.6, 3.7, and 22.6 p.p.m. If the possibility of adsorption by the crucible is disregarded (the first part of each filtrate having been discarded) the actual concentration of dissolved metaphosphate required for stabilization may be but a small fraction of that calculated from the amount added.

It was found that addition of 1150 p.p.m. of sodium hexametaphosphate resulted in disappearance of the turbidity and that maximum turbidity occurred at about 600 p.p.m. This precipitation and redissolution is in accord with the formation of soluble complex ions in other inorganic systems. The untreated synthetic water, the five turbid waters, and that containing 1150 p.p.m. were used in the permeability study. In addition, metaphosphate was added to distilled water in the same concentrations, and sodium chloride was added to the synthetic water in an amount equivalent to the sodium in 1150 p.p.m. of sodium metaphosphate (11.3 m.e. per liter).

The soil was passed through a 1-mm. sieve and uniformly packed into No. 2

tinned cans modified for permeability measurements. The 200 gm. of soil in each can occupied a height of about $1\frac{3}{4}$ inches. The hydraulic head was maintained constant by a constant-level device in conjunction with a 5-gallon supply carboy. Room temperature was maintained at $70 \pm 1^\circ\text{F}$. The permeabilities,

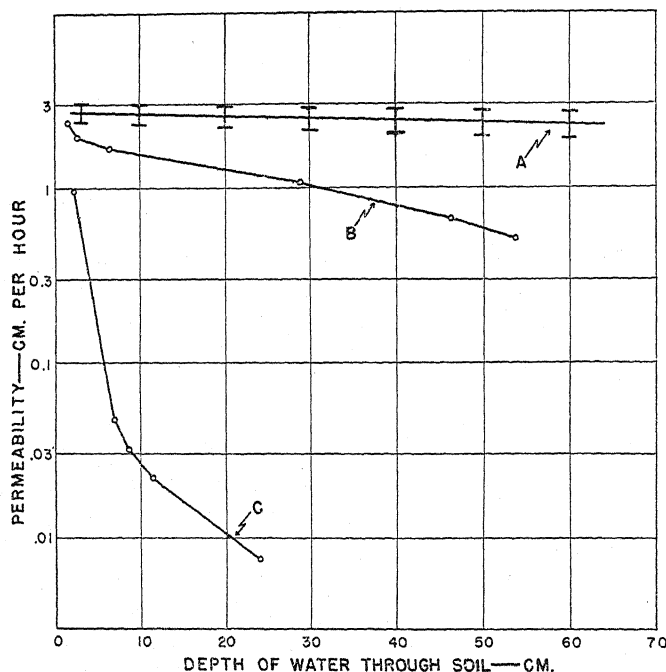


FIG. 1. PERMEABILITY OF A SAMPLE OF FALLBROOK LOAM TO WATERS CONTAINING SODIUM HEXAMETAPHOSPHATE

Range A includes curves for synthetic waters containing 0, 1, 2, 4, 10, and 100 p.p.m. of $(\text{NaPO}_3)_6$ and that containing 11.3 additional m.e. of NaCl per liter. B is curve for synthetic water containing 1150 p.p.m. $(\text{NaPO}_3)_6$. C is curve for 1150 p.p.m. in distilled water.

expressed in centimeters per hour, were calculated from the following form of the Darcy equation (2, 15):

$$P = \frac{Q}{T} \cdot \frac{1}{A} \cdot \frac{L}{H}$$

where P is the Darcy coefficient of permeability, Q is volume of percolate, T is time, A is cross-sectional area, L is height of soil, and H is hydraulic head.

The permeability results are shown in semilogarithmic graphical form in figure 1. The permeability of the soil to all the waters, including the controls (no sodium hexametaphosphate), decreased during percolation, an effect typical of most soils on prolonged leaching. Each treatment was replicated 3 to 18 times. Range A in figure 1 includes the curves for all replicates of all synthetic waters except the 1150 p.p.m. $(\text{NaPO}_3)_6$ water. The variation among replicates was

sufficient to preclude assigning a significant reduction in permeability to any of these treatments.

The 1150 p.p.m. treatment, however, reduced percolation, and after passage of 50 cm. of water (2150 ml.) the permeability was one-fourth that of the control. The curves for the lower concentrations of metaphosphate in distilled water are not shown, but they would lie between range A and curve B, the permeability decreasing with increasing metaphosphate content. The outstanding reduction in permeability resulted from the addition of 1150 p.p.m. to distilled water. After percolation of 24 cm. of this water (1030 ml.) the permeability was $\frac{1}{300}$ that of the synthetic water control. This percolate was dark from suspended clay extracted from the soil; those from the other waters that caused reduced permeability contained lesser amounts of clay. This observation illustrates the effectiveness of hexametaphosphate in dispersing soils preparatory to mechanical analysis (14). Reduction of the viscosity of oil-well drilling muds by hexametaphosphate also has been attributed to increased dispersion (3).

The results indicate that the percolation of waters stabilized by 1 to 5 p.p.m. of sodium hexametaphosphate should not affect soil permeability. At higher concentrations, the calcium-ion activity is reduced, and in waters containing an excess of the metaphosphate it becomes negligible. This results in an exchange of sodium ions for calcium ions adsorbed on the clay, with a resultant increase in dispersion and decrease in permeability.

Effect of metaphosphate on exchangeable base status

On completion of the permeability measurements, eight of the soil samples and the original soil were subjected to exchangeable base determinations. The wet soil samples were drained of excess water by suction, and the solution so extracted was used for determination of soluble salts. The top one-third of each sample was divided into two roughly equal parts. One part was reserved for base replacement and the other used for a moisture determination. A sample of the original soil was moistened to the saturation percentage (16) and treated similarly. To each exchangeable base sample was added 100 ml. of neutral normal ammonium acetate, the mixture shaken for 1 hour, centrifuged, and the supernatant liquid decanted. This procedure was followed three times. Aliquots of the composited washings and of the soluble salt filtrates were analyzed for calcium, magnesium, and sodium by the methods previously indicated, and for manganese by titration with ferrous ammonium sulfate of the permanganate formed on oxidation by sodium bismuthate. The cation contents in the filtrates were subtracted from the totals to obtain the exchangeable base values. These were then calculated on the basis of milliequivalents per 100 gm. oven-dry soil, and are reported in table 2.

The percolation of the calcium-sodium-chloride synthetic water removed the exchangeable magnesium from the soil and replaced it with calcium, and to a slight extent with sodium. Metaphosphate in concentrations of less than 100 p.p.m. caused no measurable change in calcium-sodium ratio as compared with that of the control. This was true even of the soil sample through which 340

cm. of the 2 p.p.m. water had percolated. Above 100 p.p.m. the adsorbed sodium increased, and at 1150 p.p.m. it represented 20 per cent of the adsorbed bases. This is not due to the sodium in the metaphosphate salt, however, because the addition of an equivalent amount of sodium chloride to the synthetic water did not increase the exchangeable sodium. The reduced base-exchange capacity of the sample treated with the water containing 1150 p.p.m. evidently resulted from removal of clay from the soil by the percolate during the permeability measurements. Treatment with 1150 p.p.m. of sodium metaphosphate in distilled water resulted in an exchangeable sodium percentage of 62 and an exchange capacity of only 72 per cent of that of the original soil; the increase in exchangeable manganese due to this treatment and to the percolation of 340 cm. of water is attributed to prolonged immersion of the soil. These results are in excellent

TABLE 2

Effect of sodium hexametaphosphate in the percolation water on the exchangeable bases of Fallbrook loam

COMPOSITION OF WATER			PERCOLATE*	EXCHANGEABLE BASES†				
CaCl ₂	NaCl	(NaPO ₃) ₆		Na	Ca	Mg	Mn	Total
<i>m.e./l.</i>	<i>m.e./l.</i>	<i>p.p.m.</i>	<i>cm.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
8.4	5.6	0	61.3	0.4	12.8	tr	0.2	13.4
8.4	5.6	2	67.8	0.4	12.6	tr	0.0	13.0
8.4	5.6	2	340	0.4	12.7		0.4	13.5
8.4	5.6	10	62.7	0.4	12.4	0.3	tr	13.1
8.4	5.6	100	65.0	0.5	11.7	0.1	0.1	12.4
8.4	5.6	1150	56.0	2.2‡	8.5	0.1	0.1	10.9
8.4	16.9	0	66.2	0.4‡	12.2	tr	0.2	12.8
0.0	0.0	1150	24.0	5.9‡	3.0	0.0	0.6	9.5
Original soil.....			0	0.2	11.4	1.6	0.0	13.2

* These values multiplied by 43 equal percolate volumes in milliliters.

† Per 100 gm. oven-dry soil.

‡ Difficult to determine accurately because of high soluble sodium.

agreement with the permeability determinations and demonstrate that metaphosphate can be used at the low concentrations employed in threshold treatment without affecting the exchangeable bases of a soil.

SUMMARY

Alkaline soil solutions and waters containing appreciable concentrations of calcium and bicarbonate ions can be stabilized against the precipitation of calcium carbonate by the addition of 2 p.p.m. of sodium hexametaphosphate. The storage of such solutions for analysis or for long-time soil experiments is thereby facilitated.

This concentration of metaphosphate in percolation waters apparently has no effect on the permeability and base status of a soil, as demonstrated by laboratory permeability studies and exchangeable base determinations. Much higher con-

centrations of metaphosphate cause an increase in adsorbed sodium and a corresponding decrease in permeability by virtue of the ability of the metaphosphate to form stable soluble complexes with calcium.

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THE DEPENDENCE OF FIELD CAPACITY UPON THE DEPTH OF WETTING OF FIELD SOILS¹

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The *field capacity* of a soil represents the practical upper limit of field soil moisture under conditions of unobstructed drainage. It is generally understood (8) to be the moisture content of a soil when, following a wetting from above by rainfall or irrigation, downward water movement has almost ceased. Shaw (7) has defined a similar value, the *normal moisture capacity*, more functionally as the moisture content attained during soil drainage when the water films on the soil particles have become so thin that reduced permeability permits negligible further moisture decrease in the liquid state. In practice, the terms are essentially synonymous. Neither represents an equilibrium soil moisture condition. The *field capacity*, as it will be referred to hereafter, represents merely a point on the moisture-drainage-time curve at which the drainage rate has become so low that in comparison with early rates it is insignificant. In well-drained soils of at least moderate permeability the field capacity is considered to have been reached two or three days after an irrigation, and in much agricultural literature the soil moisture content at this time is taken as a measure of the field capacity.

In a recent analysis of soil moisture data obtained on the San Dimas Experimental Forest (4) in southern California, it was found that the moisture content of the top foot of soil was increased less by rains occurring when the soil was initially dry than when the soil was initially moist to some depth. The field capacity of the soil thus seemed to depend upon the depth of soil wetting. If this is so, field capacity must be a function of the amount of water applied to the soil as well as of soil texture, structure, and profile characteristics. Since field-capacity measurements were being used in calculations of the water-retaining capacity of watershed soils, it was desirable to learn to what extent depth of wetting influenced the determination and whether some minimum wet depth could be established on which to base a reliable value.²

MATERIALS AND METHODS

The present study was made under two conditions. First, the moisture distribution through the wet soil was determined from field samplings made early in the rainy season 1 to 4 days after periods of rain. This provided data of pro-

¹ The field and laboratory work was performed by Wayne Hanawalt and Clarence Burck of Civilian Public Service Camp No. 76, Glendora, California. Their suggestions aided materially in the development of the study. Grateful acknowledgment for critical review of this paper is made to J. Kittredge, C. J. Kraebel, P. B. Rowe, C. R. Hursh, F. J. Veihmeyer, J. E. Christiansen, and G. B. Bodman.

² Implications of the field-capacity variations mentioned are contained in data obtained by Veihmeyer and Hendrickson (8) during the moisture sampling of freshly irrigated soils. Their results show a decrease in relative wetness within the wetted zone with increasing depth below the soil surface.

gressively deeper moisture penetration caused by natural rain. To supplement these data metal frames 6 square feet in area were pressed 4 inches deep into the surface soil at selected field locations to form irrigation checks, and various amounts of water were impounded in them to wet the soil to different depths. Following each irrigation the distribution of moisture through the wetted soil was determined daily for a week on auger samples taken in the middle of the irrigated area. In both phases of this study, the soil moisture before irrigation was at or below the wilting point—a characteristic of these soils at the start of the rainy season. In the study involving natural rainfall no provision was made to minimize evaporation or transpiration. In the irrigation phase of the study, heavy canvas covers were laid over the soil during the drainage period to decrease evaporation, but roots of plants not covered by the canvas were free to remove water for transpirational use.

The soils studied included three natural soils and one artificially mixed uniform soil. The natural soils are fairly representative of the more uniform alluvial and older residual soils of the experimental forest. The Tanbark Creek and Hummingbird Spring soils are sandy loams that have been transported by water to their present positions bordering the channels of intermittent streams. Because of their youth, they show no development of horizons other than some darkening near the surface, the result of organic matter accumulation. The runoff plot soil is a hillside residual clay loam which has been modified to some extent by colluvial action. It occupies one of the older geologic surfaces of the forest but shows only slight development of a clay-enriched B horizon. The soil is rich in organic matter within the top few inches, the resulting dark color gradually fading to the normal reddish yellow of the soil at a depth of about 12 inches. The field capacities of the alluvial soils lie between 10 and 13 per cent, and that of the residual soil decreases from 25 per cent at the surface to 17 per cent at 18 inches and to 15 per cent at the 60-inch depth. All three soils are more than 6 feet deep and are underlain by fractured metamorphosed dioritic rock.

The artificially mixed soil occupies a pit 3 feet deep and 110 square feet in area dug in natural soil of the same kind near a group of lysimeters. It was prepared 6 years prior to this study and has been occupied by chaparral vegetation ever since. The pit soil, a clay loam, is as uniform as repeated mixing can make it, and the natural soil beneath it is more than 6 feet deep and at least as permeable as the filled soil. The field capacity of the pit soil is about 19 per cent.

The irrigated soils showed no significant moisture changes between the second and the fifth day after irrigation. Since the moisture contents during this period were well below those corresponding to pore-space saturation, any rapid drainage that may have occurred must have taken place within the first 24 hours. In some cases losses due to transpiration began to be evident after the fifth day of drainage. In order to minimize the influence of this factor, data from the first 4 days only were analyzed.

RESULTS

Field-capacity determinations based on wetting by rains

Figure 1 shows the soil-moisture distributions in the Tanbark runoff plot determined within 4 days after early season storms totaling more than $\frac{1}{2}$ inch of

rain. Sampling was carried into summer-dry soil below the freshly wet zone; the dry soil increased from 5 to about 8 per cent moisture with increasing depth. The estimated field-capacity line drawn on the figure was obtained from the average moisture distribution after the soil had been wet at least 6 feet deep. Variations of 2 or 3 per cent in moisture about the field-capacity line may be attributed to soil heterogeneity.

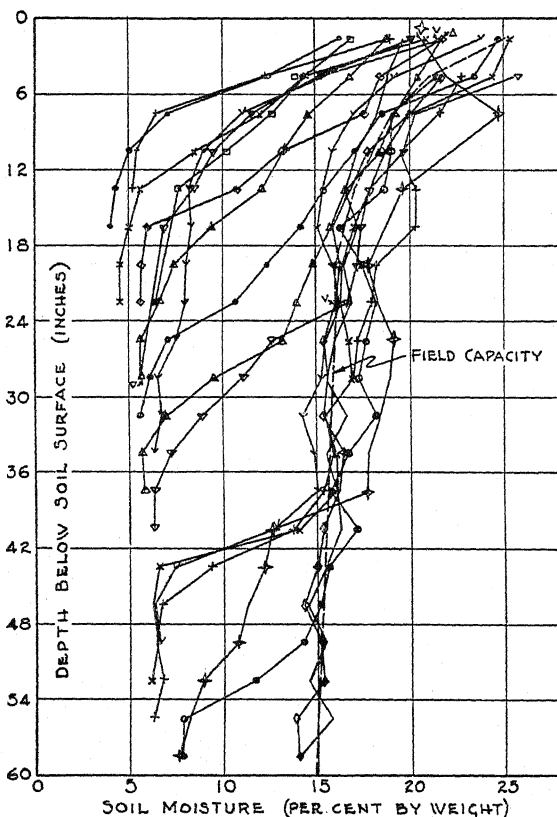


FIG. 1. SOIL-MOISTURE-DEPTH RELATIONS 1 TO 4 DAYS AFTER EARLY-SEASON STORM AT TANBARK RUNOFF PLOTS, 1940-1942

Average field capacity indicated by broken line. Each line represents the moisture distribution after a storm. Wet depths are least in September, greatest in January. Initial soil moisture (vertical section of lower ends of curves) increases from 5 to 8 per cent with depth.

The data show that until water has penetrated about 30 inches deep the moisture content at any stated depth within the wet zone increases with penetration of the wet front. The zone in which the moisture content is thus a function of wet depth will be referred to as the *wetting zone*. When the soil is wet below the 30-inch depth, first the surface layers and then successively deeper layers reach maximum moistures unaffected by further downward penetration of moisture. The wetting zone thus moves downward in the soil as the depth of moisture penetration increases.

In figure 2 the same data have been plotted in such a way as to demonstrate, first, the presence of the wetting and constant moisture zones, and second, the change in thickness of the wetting zone in relation to the depth of the sampled soil layer. Here the moisture content of each layer is plotted in relation to its height above dry soil. Thus it shows the change of moisture in each layer as the soil is wet progressively deeper below it. The wetting zone is shown to be present for all depths of soil wetting; that is, there is no depth of wetting at which the maximum field capacity is found, 1 to 5 days after irrigation, immediately above the wet-front plane. The thickness of the wetting zone is shown to decrease, however, as the wet depth increases. Thus the surface soil first reaches its maximum moisture value when the soil has been wet 30 inches deep, whereas the 30-inch layer reaches its maximum with dry soil at a depth of 42 inches below the surface, representing a wetting zone thickness of only 12 inches.

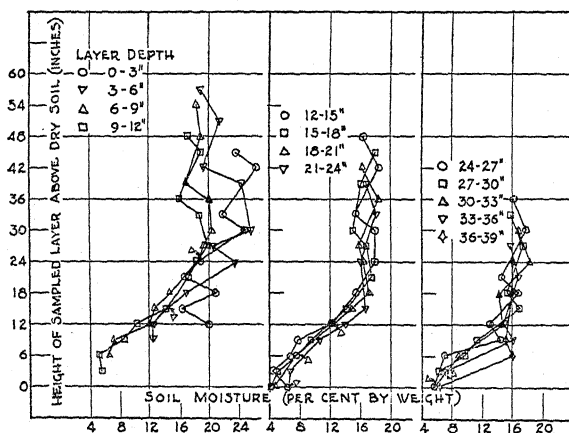


FIG. 2. SOIL MOISTURE DATA FROM FIGURE 1 REPLOTED TO SHOW RELATION OF MOISTURE CONTENT OF EACH LAYER TO ITS HEIGHT ABOVE DRY SOIL

In figure 3 the moisture contents have been expressed as percentages of the field capacities shown by the broken line in figure 1. By the use of this device changes in field capacity at different depths have been eliminated, and the progressive decrease in wetting zone thickness with increasing depth of soil is shown more clearly. In this figure the curves for successive layers have been shifted progressively to the right to avoid the confusion of overlapping data. The top of the wetting zone is shown by the abrupt change in slope of the individual moisture curves, and the line connecting these points demonstrates the decreasing thickness of this zone in relation to increasing layer depth.

Field capacity measurements based on artificial irrigations

Figures 4, 5, and 6, present, in the same manner as figure 3, moisture distribution in relation to wet depth for the three irrigated soils of the Tanbark Creek, Hummingbird Spring, and Lysimeter Pilot plots respectively. Here moisture

rather than percentage of field capacity is plotted as the abscissa, because of the general textural uniformity of these soils, and the circled points in the figures denote the top of the wetting zone. Figures 4 and 5 present the data for undisturbed field soils which have field capacities averaging 10 per cent and 13 per cent moisture, respectively, whereas figure 6 shows results obtained by irrigation of artificially mixed uniform soil which has a field capacity of about 19 per cent.

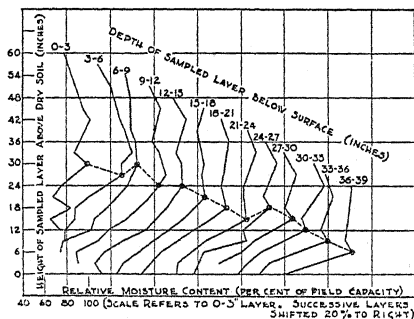


FIG. 3

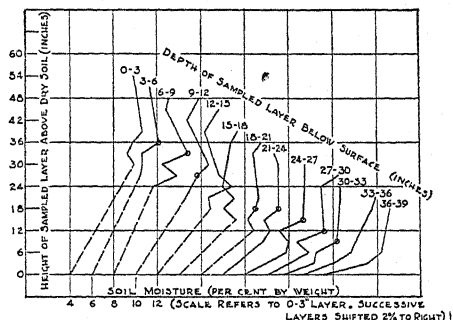


FIG. 4

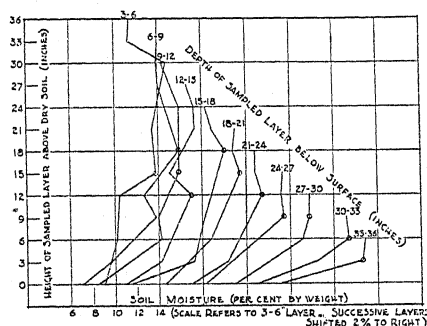


FIG. 5

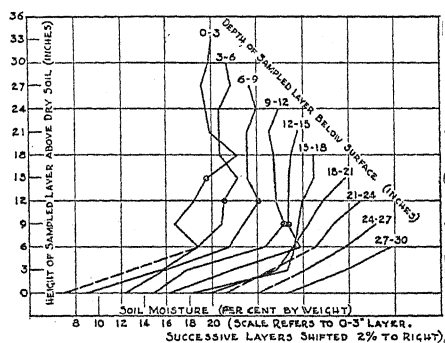


FIG. 6

FIGS. 3, 4, 5, 6. SOIL MOISTURE IN RELATION TO HEIGHT ABOVE DRY SOIL, PLOTTED TO DEMONSTRATE THE PRESENCE AND TREND OF THE WETTING ZONE 1 TO 4 DAYS AFTER IRRIGATION

Broken lines connect initial (dry) moisture content to that determined within the wet zone closest to the dry soil

The surface soil on the Tanbark Creek plot is shown to have reached its maximum moisture value only when the soil was wetted to a depth of at least 30 inches. This is in general agreement with the data shown in figure 1, obtained under natural rainfall conditions in a soil of considerably higher field capacity. The decreasing thickness of the wetting zone likewise agrees in the two plots, lending some assurance to the belief that the findings reported earlier were not accidental.

Figure 5 shows the wetting zone to be thinner at all depths on the Hummingbird Spring plot (note that the ordinate scale of figures 5 and 6 is not the same as

that of figures 3 and 4), but there is still some decrease in wetting zone thickness with increasing wetted depth.

Evidence is presented in figure 6 that the wetting zones found on the other plots are not the result of having used natural, nonuniform soils. As was mentioned earlier, the Pilot Plot soil had been made as uniform as possible by repeated mixing and then placed in a pit underlain by natural pervious soil of the same kind. The moisture distribution data again show the presence of a wetting zone, which in this case extends at least 15 inches below the surface soil. The decrease in wetting zone thickness in response to increasing layer depth is still evident but is not so definite here as in figures 4 and 5.

DISCUSSION

No measurements have been made to indicate the reasons for the wetting zone forms, which seem to be characteristic of the soil irrigations reported. A tentative explanation, however, based on knowledge of the stored volume of soil water, water moving forces, and liquid permeability conditions within the wet soil, is offered.

The downward movement of soil water takes place in response to the combined pressure potential and gravitational potential gradients operating within the soil, as has been demonstrated by Bodman (1). He has pointed out that during irrigation of soil in part saturated and in part unsaturated, the pressure-potential gradient, corresponding to the soil-moisture gradient, forms the major part of the total potential gradient. It has been demonstrated further in field studies by Edlefsen and Bodman (3) and in laboratory studies by the author³ that during and very shortly after irrigation the moisture content of the greater part of the wet zone is well above its field capacity, the moisture equivalent being taken as an approximation of this value (2). The removal of free water from the surface of an irrigated soil does not result in the cessation of downward movement of water already in the soil if unimpeded drainage is provided. The pressure potential gradient developed during irrigation still supplements the gravitational potential gradient, at least if the wet zone is underlain by drier soil. Total potential gradients causing downward flow are, therefore, still in evidence. Further downward movement now takes place at the expense of water stored in the upper part of the moist zone, and as a result, two processes come into play to decrease the rate of downward flow: first, a decrease in average moisture gradient in the wet zone results in a decrease of its average pressure potential gradient; and second, the decreasing moisture content of the wet zone soil results in decreasing liquid permeability (capillary conductivity). The rapid drop in liquid permeability of soil as its moisture content decreases from pore-space saturation has been shown by Moore (5), Richards (6), and other workers.

Since both pressure potential gradients and permeabilities within the soil decrease with time, the process of drainage of an irrigated soil is self-degenerative. The rate of downward water movement, therefore, may eventually become in-

³ Colman, E. A. *Interrelations of Soil and Water During Infiltration*. 1942 (Doctoral thesis, University of California.)

significantly small when compared with movement in other directions induced by temperature gradients (3) and those evaporative water losses that cannot be prevented.

The influence of initial depth of irrigation water penetration upon the moisture content of the drained soil may be rationalized in the light of permeabilities and potential gradients found therein. At the time of cessation of irrigation, the pressure potential at the soil surface is constant, regardless of wet soil depth. The same can be said for the dry soil immediately below the wet front and also, as has been shown elsewhere by the author,³ for the moist soil at the wet front plane. With pressure potential values, and therefore moistures and permeabilities, fixed at both top and bottom of the wetted soil column, the only difference in characteristics of these columns appears to be that of depth of moisture penetration. The average permeability of such soil columns differing only in wet depth would thus be the same, but the average pressure potential gradient would be inversely proportional to the depth of irrigation penetration. At the same time the pressure potential difference across the wet front would be the same regardless of wet depth.

It appears then that at the inception of drainage the wetting of dry soil below the wetted zone would go on at a rate independent of the wet depth, whereas the rate of downward water movement within the wet zone would be slower the greater the initial depth of wetting.

Although at the inception of drainage the wet fronts of both soils would move downward at the same rate, the more deeply irrigated soil shortly would fall behind the other because of less rapid replacement of water at its wet-front plane, a condition resulting in a more rapid decrease of pressure potential difference between wet and dry soil. The degenerative action of soil drainage already discussed would finally result in both soils' reaching insignificantly slow rates of moisture decrease, but the moistures found in the shallow and deeply irrigated soils at this time would be significantly different. Because of the higher average pressure potential gradient in the wetted zone of the less deeply irrigated soil, the moistures there would reach lower values (lower values of liquid permeability) at the cessation of drainage than would be the case in the more deeply irrigated soil with its less rapid initial delivery of water to the wet front.

SUMMARY

The field capacity is a useful definitive characteristic of a soil. In this paper the determination of field capacity by natural and artificial irrigation of mountain soils *in situ* and of a mixed, uniform soil, has shown that these soils must be wetted 12 to 30 inches deep, depending on the soil studied, before the surface layer will have attained a moisture content as high as its field capacity. Subsurface layers are shown to have lesser wetting zone thicknesses, but soil as deep as 30 inches is not raised to its maximum moisture until the wet front has penetrated from 36 to 42 inches below the soil surface. A tentative explanation is presented, relating the field-capacity values to the water supply available for drainage and the distribution of permeability and moisture potential gradients through

the wet zone at the time when the drainage rate has become insignificantly small.

This study suggests that shallow field irrigations or the irrigation and drainage of short soil columns in the laboratory do not necessarily provide valid measures of the field capacity of a soil.

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THE TRANSLOCATION OF POTASSIUM AMONG PEACH ROOTS¹

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Numerous investigations have dealt with potassium fixation in soils and with the very slow or negligible movement of potassium salts through some of them. Pomologists, in particular, have been interested in this problem. McKinnon and Lilleland (5) were concerned with a very high capacity for potassium fixation and its subsequent limitation of the penetration of potassium into some California orchard soils. In order to provide potassium to the roots in the upper 3 feet of soil, solutions of potassium salts were injected through specially constructed rods by means of pressure provided by an orchard sprayer. Mathews (7) reported work on the injection of potassium and phosphorus into Indiana peach orchard soils, in which equipment similar to that described by McKinnon and Lilleland was used.

Wander and Gourley (10), in an investigation of the possible relationship between potassium fixation in certain orchard soils and the occurrence of a type of leaf scorch on apple trees, studied the vertical penetration of potassium applied to the surface of Ohio apple orchards. They found only very slight movement of this nutrient below the top 6 inches in sod or in cultivated soils. Under an organic mulch, however, potassium was found to penetrate in considerable quantities to depths of 24 to 32 inches.

Nightingale, Schermerhorn, and Robbins (8) and Janssen and Bartholomew (4) showed that potassium remains water-soluble and is translocated freely through the tops of plants from mature or nearly mature tissues to regions of active growth. Mason and Maskell (6) found that potassium is translocated from the top of cotton plants to the roots. They suggested, moreover, that the return of potassium and other inorganic nutrients to the roots influences the absorption of additional nutrients by the roots.

If potassium is translocated freely from one region of growth to another through the tops of plants, or from the tops to the roots, why should we not expect this mobile nutrient to be translocated upward or downward through roots in response to the stimulus of actively growing tissues wherever such tissues may occur along the same vascular track? On the other hand, we have little reason to expect much cross-transfer of potassium from roots emerging from one side of the root system to those emerging from the other side, especially in tree roots, since Auchter (1) and others found that cross-transfer of nutrients from roots emerging on one side of fruit trees to the branches on the other side takes place only to a minor degree. But if potassium is translocated from one part of a root system to another, then surface soil applications of this nutrient, if absorbed by roots in that area, might be expected to provide potassium to the whole tree.

¹ Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, division of horticulture.

We have precedent to anticipate such translocation through roots in the excellent work of Breazeale (2), who demonstrated that wheat plants absorb water from any soil horizon in which moisture is available and may transport it to another horizon in which a deficiency of moisture exists. Breazeale also demonstrated that sufficient water may be translocated from roots provided with moisture to other roots in soil maintained below the wilting percentage and that the latter roots may exude this water in amounts sufficient to enable the absorption of nutrients from the relatively dry soil.

PLAN OF INVESTIGATION

In June, 1938, preliminary experiments were conducted to determine whether potassium is translocated from an upper tier of roots, corresponding to roots in a surface soil, to a lower tier of roots, corresponding to those in a B horizon or in a subsoil. For this purpose only two extremely potassium-deficient 1-year-old peach trees were used. The progress of potassium translocation in the roots of these trees was followed by means of microchemical tests on free-hand sections of representative root samples examined under a microscope.

The definite evidence of potassium translocation obtained from the 1938 studies prompted a series of experiments conducted the following summer on a scale adequate to enable the movement of potassium among roots to be estimated quantitatively. An abstract of some of this work was published in 1941 (3).

Description of double-chambered cultures

In order to study the movement of potassium vertically from one tier or layer of roots to another, it was necessary to prepare special double-chambered cultures in which the roots might be placed in inert sand and supplied with nutrients with the possibility of contamination from one chamber to another reasonably precluded. Such containers were easily prepared from a combination of an 8-inch standard clay pot and a glazed earthenware crock. The clay pot was drilled at the intersection of the bottom and the wall to accommodate a no. 3 rubber stopper. The bottom drain hole was enlarged by filing to permit a glass tube 1-inch in diameter and 7 inches long to be sealed securely in place within the clay pot by a specially bored no. 8 rubber stopper. After the pot was drilled and filed, it was given two coats of Bakelite varnish on all surfaces. In the 1939 and subsequent experiments, the pots were given a final coat of aluminum paint on the outside in order to minimize the absorption of heat.

Roots to be placed in the bottom chamber were inserted through the glass tubing in the center of that chamber. Only roots of sufficient length for this purpose could be used. A piece of small, heavy-walled glass tubing extended through the side of the top chamber and was connected by means of thick-walled rubber tubing to another piece of heavy-walled glass tubing which extended through the drain hole in the bottom chamber. The latter tube was made to extend through the drain sufficiently far to preclude any contamination to the bottom of the culture. Adjustment of the length of rubber tubing used to connect the drain from the top chamber enabled this chamber to rest firmly and uprightly on the sand in the bottom chamber.

The upper chamber was filled with sand to a level approximately $\frac{1}{2}$ to $\frac{3}{4}$ inch below the top of the glass tube.

Plant material

One-year-old dormant nursery peach trees with long taproots were selected, and side roots were removed in order to stimulate the development of new flexible ones of fairly similar size. The trees were planted in washed white sand, in tall, 3-gallon, glazed crocks and were supplied with a potassium- and ammonium-free nutrient solution. When the trees showed symptoms of potassium deficiency, the roots were carefully washed out of the sand and the plants were transferred to double-chambered sand cultures.

Since it has been demonstrated that the cross-transfer of nutrients takes place only very slowly in fruit trees, roots were selected in such a manner that one in the lower half was paired with one of similar size directly above it in the upper half of



FIG. 1. ONE-YEAR-OLD PEACH TREES GROWING IN DOUBLE-CHAMBERED SAND CULTURES

the root system. Four or more roots $\frac{1}{16}$ to $\frac{1}{8}$ inch in diameter were selected in each half, and all others were removed. The lower half of the root system was passed through the glass tube in the center of the top chamber and was then distributed as widely and deeply as possible in the sand of the bottom chamber. Peach trees with their roots divided between the two chambers are illustrated in figure 1.

In order to compensate for the decreased size of the root system, the tops of the trees were severely cut back at the time the roots were pruned and distributed in the double-chambered cultures.

All plants were supplied daily with applications of a potassium-free nutrient solution until symptoms of severe potassium deficiency developed. At this time different nutrient treatments were applied to allow a study of potassium translocation. Considerable care was required in the application to the top chambers of nutrient solutions containing potassium in order to avoid overflow through the center tube, thus contaminating the sand in the bottom chamber. Wash

bottles were used to apply the solution when the treatments required the addition of potassium to top chambers.

Nutrient solutions

Only two nutrient solutions were required for this study: (a) a "complete" solution containing 0.0045 M $\text{Ca}(\text{NO}_3)_2$, 0.0036 M KH_2PO_4 , and 0.00237 M MgSO_4 , and (b) a potassium-free solution containing 0.0045 M $\text{Ca}(\text{NO}_3)_2$, 0.0036 M NaH_2PO_4 , and 0.00237 M MgSO_4 . Minor elements were added to both solutions in the following concentrations: 1.0 p.p.m. Mn, 0.3 p.p.m. B, 0.05 p.p.m. Zn, and Fe in amounts varying from 0.1 to 10 p.p.m. depending on the prevalence of iron-deficiency chlorosis. Ammonium nitrogen was omitted from the nutrient solutions to avoid interference with potassium tests and analyses.

Procedure for 1939 experiments

A group of 32 carefully selected peach trees, already established in double-chambered cultures, and all showing symptoms of severe potassium deficiency, were divided into the following treatments: series I, control trees to which a potassium-free nutrient solution was applied in both root chambers; series II, trees to which a complete solution was applied to the top chamber and a potassium-free solution to the bottom; and series III trees to which a potassium-free solution was applied to the top chamber and a complete solution to the bottom.

Trees were harvested 5, 13, and 43 days after application of potassium to one of the chambers. The first harvest consisted of four trees from each of series I and II showing the most severe foliar symptoms of potassium deficiency. Subsequent harvests comprised four trees from each series. At the time of the second harvest, two trees in series I showed symptoms of extreme potassium deficiency, and these were sampled separately from the other two trees. Similarly, two of the trees selected from series II at this time showed more advanced symptoms of potassium deficiency than the other plants chosen and, therefore, they were sampled separately.

The trees were aliquoted into terminal 6-inch portions of stems, fleshy and fibrous roots less than $\frac{1}{16}$ inch in diameter from top chambers, and corresponding root samples from bottom chambers. Only live roots were included. All samples were dried rapidly at 73°C. with forced air circulation. The samples were ashed and analyzed for potassium, calcium, and magnesium. All results were calculated on a dry-weight basis. The values for root analyses were calculated on a silica-free, dry-weight basis.

Each culture was examined carefully for evidence of leaks whenever roots were removed, but none were found. Moreover, the sand from one or more bottom chambers of series II was leached at each harvest period, and the leachate was tested for potassium. In all instances, negative results were obtained.

RESULTS AND DISCUSSION

The young peach trees used for the preliminary studies were so deficient in potassium that severe foliar necrosis and stunting of growth were very evident,

and nearly all of the potassium present in the fleshy roots was found in the phloem tissues. Only rarely was more than one crystal of $K_2NaCO(NO_2)_6$ found in any phloem cell. In general, not more than one out of 50 cortical cells contained potassium. Some fibrous roots contained potassium in xylem cells as well as in the phloem.

One day after potassium was added to the top chambers, root samples comparable to those examined the previous day were removed from the bottom chambers and tested for potassium. Many of the fleshy roots contained more than one crystal of $K_2NaCO(NO_2)_6$ in the phloem. An increase over that found the previous day was apparent in most sections examined, indicating that some movement of potassium from the top roots had already occurred. No change in the potassium content of either the cortex or xylem could be detected at this time, however.

After five daily applications of a complete nutrient solution had been given to the top chambers, while a potassium-free solution was applied to the bottom ones, root samples were again tested microchemically. Fleshy roots from the bottom chambers at this time showed an abundance of potassium in the stele. Cortical cells usually contained at least one or two crystals of $K_2(NaCO(NO_2)_6)$, and some showed as many as 14. It was evident from these results that potassium was being adsorbed by the roots in the top chamber and translocated in considerable amounts to the potassium-deficient roots in the bottom chamber.

After 41 days the cultures were taken apart. The sand in the bottom chambers was leached, and the leachate, after concentration to a small volume, was found to be free of potassium. The roots in the bottom chambers (fig. 2) were found to have made slightly better growth than those in the top chambers. This was due undoubtedly to the higher and less favorable temperature that prevailed in the red, moisture-proof pots as compared with that in the large, white, bottom chambers. The new growth on bottom root systems showed no signs of inadequate potassium supply. That the roots in the top chambers alone were able to absorb an adequate supply of potassium for good growth is illustrated by the tree shown in figure 3.

The progress of potassium translocation among roots of the 1939 experiments is best illustrated by a comparison of figures 4, 5, and 6. In figure 4 it may be seen that roots to which potassium was supplied absorbed the nutrient rapidly and that a small amount of it was transported to roots in the bottom chambers. That the small increase in potassium content of roots in the bottom chambers, as compared with that found in series I, is significant as indicated by the trend shown in figures 5 and 6. Strong support to the values in figure 4 is also furnished by the marked increase in potassium found in the stele and cortical cells on the fifth day of the 1938 experiments.

Figure 5 shows that by the 13th day very marked increases in potassium content were found as a result of translocation from roots supplied with a complete nutrient solution. With continued absorption, moreover, the amounts translocated to roots receiving no external supply of potassium gradually increased, as shown in figure 6.

The minimum content of potassium for normal root activity in peaches has not been established. It is probably safe to predict that the figure for fleshy and

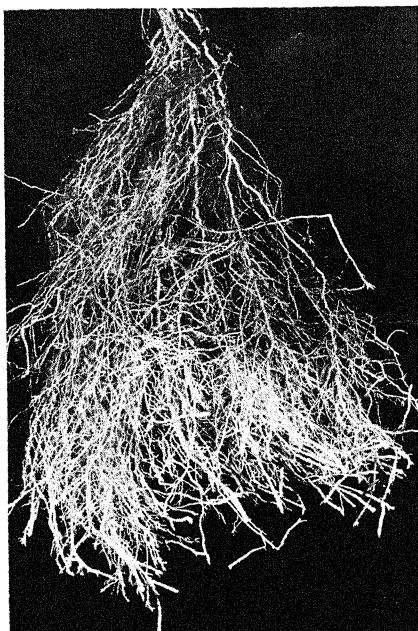


FIG. 2

FIG. 2. PEACH-TREE ROOTS FROM LOWER CHAMBER IN 1938 EXPERIMENTS 41 DAYS AFTER POTASSIUM WAS APPLIED TO TOP CHAMBER

An abundance of new, active roots has been developed as a result of potassium translocated from above



FIG. 3

FIG. 3. ONE-YEAR-OLD PEACH TREE FROM 1938 EXPERIMENTS, SHOWING TOP GROWTH 41 DAYS AFTER POTASSIUM WAS APPLIED TO UPPER CHAMBER

Symptoms of potassium deficiency are evident on the old foliage near bases of lower branches

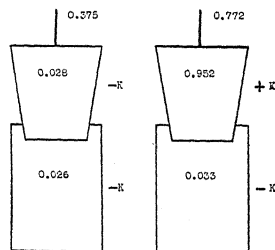


FIG. 4. POTASSIUM CONTENT, AS PER CENT OF DRY WEIGHT, 5 DAYS AFTER SHIFT TO PLUS-POTASSIUM TREATMENT

small fibrous roots, however, would be less than 1.0 per cent on a dry-weight basis, since that amount of potassium in dry leaves usually has been found adequate for the peach.

Series III roots in the top chamber after 43 days contained only 0.693 per cent potassium, but they were normal in appearance and had developed considerable growth following the application of potassium to the bottom chamber.

Plant tissues usually accumulate calcium and magnesium when they contain relatively little potassium. Similarly, they usually accumulate potassium when calcium or magnesium is low. The results presented in table 1 show that as the potassium content of roots receiving none of this nutrient from the sand increases as a result of translocation, the calcium content of those roots decreases. Magnesium shows no definite trend in this respect. It is quite obvious, however,

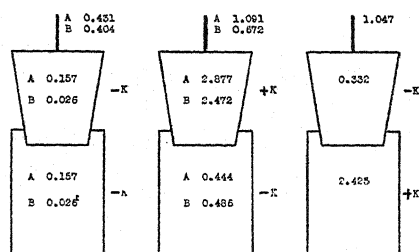


FIG. 5. POTASSIUM CONTENT, AS PER CENT OF DRY WEIGHT, 13 DAYS AFTER SHIFT TO PLUS-POTASSIUM TREATMENT

A, plants showing mild symptoms of potassium deficiency; B plants showing pronounced symptoms of potassium deficiency

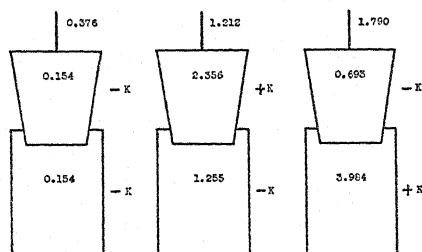


FIG. 6. POTASSIUM CONTENT, AS PER CENT OF DRY WEIGHT, 43 DAYS AFTER SHIFT TO PLUS-POTASSIUM TREATMENT

that when potassium is supplied to one of the root chambers of a culture, the magnesium content of the roots in that chamber decreases.

The results of these investigations do not justify the conclusion that the presence of potassium in the soil (or root medium) surrounding each root is without beneficial effects. Similarly, the excellent growth of roots with potassium provided entirely by translocation from other roots above or below them on the same tree is not conclusive evidence that a supply of potassium in the root medium around each root would not have stimulated growth even superior to that obtained in these investigations. On the other hand, it is unlikely that the subsoil of a suitable orchard site would be so devoid of potassium as was the sand in the root chambers of this study, provided as they were with potassium-free nutrient solutions.

Potter and Percival (9) have demonstrated that apple trees with an abundance of roots extending through and even to the top of the soil may quickly absorb potassium from surface applications and translocate it to the foliage. These findings are evidence of the practical application of the results reported herein.

From the results of this investigation, it may be concluded that orchard cultural practices which favor the development of extensive and active root growth in the surface soil should lead to economy and efficiency in the use of potash fertilizers. They show, moreover, that potassium absorbed by roots in the surface soil may be made available to roots in the subsoil by translocation through the

TABLE 1

Comparative potassium, calcium, and magnesium contents of peach twigs and roots grown in double-chambered cultures with different nutrient treatments

(Twig analyses are expressed on percentage of dry weight basis, and root analyses are expressed on percentage of silica-free dry weight basis)

	SERIES I			SERIES II			SERIES III		
TOP CHAMBER TREATMENT.....	Minus K			Plus K			Minus K		
Bottom chamber treatment.....	Minus K			Minus K			Plus K		
Material Analyzed.....	K	Ca	Mg	K	Ca	Mg	K	Ca	Mg
After 5 days									
Twig terminals*.....	0.375	0.878	0.207	0.772	0.889	0.376			
Top roots.....	0.028	3.725	0.278	0.952	3.807	0.337			
Bottom roots.....	0.026	3.868	0.342	0.033	4.245	0.408			
After 13 days									
Twig terminals*.....	0.431	0.818	0.228	1.091	1.269	0.229			
Top roots.....	0.404	0.749	0.264	0.672	1.099	0.235	1.047	1.130	0.295
Bottom roots.....	0.157†	2.614†	0.439†	2.877	2.282	0.324	0.332	1.992	0.487
Bottom roots.....	0.026†	4.394†	0.489†	2.472	2.301	0.305			
Bottom roots.....				0.444	3.217	0.503	2.425	1.858	0.556
Bottom roots.....				0.486	3.217	0.432			
After 43 days									
Twig terminals*.....	0.376	1.017	0.231	1.212	1.272	0.216	1.790	0.992	0.179
Top roots.....	0.154†	2.770†	0.382†	2.356	2.567	0.228	0.693	1.385	0.625
Bottom roots.....				1.255	2.371	0.467	3.984	0.929	0.346

* Tip 6 inches.

† Samples comprised top and bottom roots combined.

root systems of trees. Under such cultural practices on soils with high potassium-fixing capacity, trees may be expected to absorb this nutrient effectively from surface applications. In contrast, the results of these studies indicate that there is little, if any, justification for subsoil applications, or injections, of potash fertilizers.

SUMMARY

By the use of special double-chambered sand cultures which enabled the separation of peach roots into two distinct horizontal layers, it was possible to apply

potassium to one layer of roots without contamination of the others. The results of these studies have shown that potassium may be absorbed by one layer of roots and may be translocated vertically up or down through the root system rapidly and in considerable quantities to other roots receiving no external supply of this material.

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OVER FIVE HUNDRED REASONS FOR ABANDONING THE CROSS-INOCULATION GROUPS OF THE LEGUMES

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If an organism from the nodule of a leguminous plant will effect nodulation on another plant, the two plants are considered as belonging to the same "cross-inoculation group." From the results of such tests a series of groups have been fostered in which the root-nodule organism is mutually interchangeable. A list of 16 of these groups can be found in the studies by Fred, Baldwin, and McCoy (6) published in 1932. Since this date, the suggestion has been made that certain groups should be combined and that other groups should be added, so that at present at least twenty-two groups have been proposed. Even this number of groups did not provide for all exigencies, and the further suggestion was made that groups within groups should be arranged (1).

Within the last few years considerable doubt has arisen concerning the validity of these groups. Wilson (10, 11) concluded from the results of various workers, whose ideas he reviewed, as well as from the results of his own work, that neither a sufficient number of plant species nor a sufficient number of diverse strains of the organism had been employed by investigators, in a comparative study of the symbiotic relations as measured by nodulation and by nitrogen fixed, to justify the establishment of definite cross-inoculation groups or to encourage the use of those that have been arranged. He suggested that though the groups may be useful in a practical way, certainly from the scientific standpoint they should be abandoned. This conclusion and suggestion resulted from a study of the nodulating performances of isolates from legumes and from a study of the morphology and the physiology of the isolates. The data in this paper are presented in support of the idea that the cross-inoculation groups should be abandoned.

METHODS

Numerical list of plants employed

Seeds of various plants employed in this work were obtained from various exchanges or from the U. S. Department of Agriculture or were gathered for the particular purpose. In some cases it was necessary to grow plants to the bloom stage in order to be certain of the species. A numerical list of the plants used follows.

1. *Abrus precatorius* L., 2. *Albizia julibrissin* Biov., 3. *Amorpha canescens* (Nutt) Pursh, 4. *A. elata* Pursh, 5. *A. fruticosa* DC., 6. *A. microphylla* Pursh., 7. *Amphicarpa monoica* Ell., 8. *Anthyllis vulneraria* DC., 9. *Astragalus menziesii* A. Gray, 10. *A. Nuttalianus* DC., 11. *A. rubyi* Green & Morris, 12. *A. verus* Georgi, 13. *Baptisia australis* R. Br., 14. *Cajanus indicus* Spreng, 15. *Caragana frutecens* DC., 16. *Cassia chamaecrista* L., 17. *Coronilla varia* L., 18. *Crotalaria anagyroides* HBK., 19. *C. falcata* Vahl., 20. *C. hildebrandtii* Velka., 21. *C. intermedia* Kotschy., 22. *C. juncea* L., 23. *C. lanceolata* E. Mey., 24. *C. maxil-*

laria Klotzsch., 25. *C. mundyi* Baker., 26. *C. mysorensis* Roth., 27. *C. polysperma* Kotschy., 28. *C. sagittalis* L., 29. *C. sericea* Willd., 30. *C. silvestris*, 31. *C. spectabilis* Roth., 32. *C. striata* DC., 33. *C. usaramoensis* Baker, 34. *C. verrucosa* L., 35. *Dalea alopecuroides* Willd., 36. *Desmodium canadense* DC., 37. *D. canescens* DC., 38. *Glycine max* (L.) Merr., 39. *Laburnum vulgare* L., 40. *Lathyrus maritimus* Bigel., 41. *L. partense* L., 42. *Lens esculenta* L., 43. *Lespedeza formosa* (Vogel) Koehne, 44. *L. striata* Hook & Arn., 45. *Leucaena glauca* Benth., 46. *Lotus corniculatus* L., 47. *L. crassiflorus* Pers., 48. *Medicago lupulina* L., 49. *M. sativa* L., 50. *Mimosa invisa* Mart., 51. *Onobrychis viciaefolia* Scop., 52. *Ononis vaginalis* Vahl., 53. *Oxytropis Lambertii* Pursh., 54. *Phaseolus coccineus* L., 55. *P. vulgaris* L., 56. *Rhynchosia minima* DC., 57. *Robinia Pseudo-Acacia* L., 58. *Schrankia uncinata* Willd., 59. *Sesbania macrocarpa* Muhl., 60. *Spartium scoparium* L., 61. *Stizolobium Deeringianum* Brot., 62. *Strophostyles helvola* (L.) Britton, 63. *Swainsona coronillaefolia* Salisb., 64. *Tephrosia vogelii* Hook., 65. *Thermopsis caroliniana* M. A. Curt., 66. *Trifolium alexandrianum* L., 67. *T. ambiguum* Bieb., 68. *T. arvense* L., 69. *T. dubium* Sebat., 70. *T. fragiferum* L., 71. *T. hybridum* L., 72. *T. medium* L., 73. *T. pratense* L., 74. *T. repens* L., 75. *Trigonella Foenum-Graecum* L., 76. *Vicia faba* L., 77. *V. pannonica* Crants, 78. *V. villosa* Roth., 79. *V. villosa* var. Gore, 80. *Vigna sienensis* Endl., 81. *Wistaria chinensis* DC., 82. *W. frutescens* Rafin.

Laboratory procedure

The methods employed in obtaining evidence on which to base conclusions that the plant-bacteria groups should be abandoned were similar to those previously described (9). The symbionts were housed during the growing period in surroundings from which interfering organisms were excluded and in which fairly satisfactory growing conditions were maintained. Adequate controls were provided. The seeds of all species were immersed in concentrated sulfuric acid for an appropriate time, washed to remove the acid, treated with a solution of calcium hypochlorite (9), and planted in the flasks with the chlorine adhering to them. After an hour or so, the sterilized soil in the containers was inoculated by dropping a suspension of the desired organism over the surface by means of a pipette. The containers with the plantings were kept in a greenhouse for 30 or more days before the roots were examined for nodules.

PRESENTATION OF DATA

If the cross-inoculation groups are as inclusive and as exclusive as they are supposed to be, a plant that bears nodules after exposure to an isolate should be placed with or belong to the group from which the isolate came. This provides the boundary around the group and furnishes the necessary reciprocity and specificity which are necessary to establish the group. If the plant symbioses with isolates from other groups, or if the organism effects nodules on plants in other groups, the groups lose their value and the organism is not specific for a group. Should the isolate effect nodules on a plant outside the group or on plants in another group, it apparently has not been materially changed, for no evidence is available to indicate that an isolate, while sojourning in symbiosis with such plants, has lost its ability to symbiose again with the species from which it was originally isolated.

Performance of isolates as related to cross-inoculation groups

With such prescribed boundaries it should be easy to assign a plant to a particular group and to maintain those groups that have been arranged. The per-

formance of isolates will indicate how much confidence can be placed in the groups. The data are arranged in table 1.

It appears that the isolates employed were not specific for any cross-inoculation group. The organism from *Albizia julibrissin* symbiosed with plants that have been assigned individually to five groups. The organism from *Cassia*

TABLE 1

Performance of isolates with plants of various cross-inoculation groups and with other plants not assigned to any group

ISOLATE FROM	SYMBIOSED WITH PLANT NUMBER*	NUMBER OF GROUPS REPRESENTED	ADDITIONAL NUMBER NOT ASSIGNED†
<i>Albizia julibrissin</i>	2, 5, 38, 69, 71	5	Several
<i>Cassia chamaecrista</i>	3, 4, 5, 6, 16, 22, 35, 55, 66, 68, 69, 70, 71, 72, 73, 74	5	25
<i>Dalea alopecuroides</i>	3, 4, 5, 6, 16, 35, 55, 57, 61	6	31
<i>Desmodium canadense</i>	3, 4, 5, 6, 14, 36, 38, 55, 57, 77	7	30
<i>Glycine max</i>	5, 30, 38, 55, 57, 60	5	18
<i>Lespedeza striata</i>	3, 4, 5, 6, 10, 38, 44, 51, 55, 57, 68, 69, 70, 71, 72, 73, 74, 78	8	27
<i>Lotus corniculatus</i>	3, 22, 35, 41, 44, 46, 55, 57, 59	7	7
<i>Lupinus perennis</i>	5, 16, 35, 36, 46, 51, 55, 57, 59, 60, 76	8	12
<i>Medicago sativa</i>	5, 49, 54, 57	4	8
<i>Onobrychis viciaefolia</i>	5, 46, 51	3	6
<i>Oxytropis Lambertii</i>	4, 16, 46, 53, 55, 57, 66, 69, 71, 73, 74, 77	7	24
<i>Phaseolus vulgaris</i>	5, 8, 36, 51, 55, 57	6	11
<i>Robinia Pseudo-Acacia</i>	5, 46, 49, 51, 55, 57, 77	7	12
<i>Sesbania macrocarpa</i>	35, 55, 57, 59	4	29
<i>Stizolobium Deeringianum</i>	5, 8, 15, 35, 55, 57, 61, 62, 66	9	38
<i>Strophostyles helvola</i>	8, 28, 51, 57, 62, 73	6	11
<i>Swainsona coronillaefolia</i>	5, 16, 17, 46, 48, 55, 66	6	43
<i>Thermopsis caroliniana</i>	5, 22, 51, 55, 57, 65, 73, 78	6	8
<i>Trifolium pratense</i>	5, 22, 55, 57, 77	6	27
<i>Vicia villosa</i>	5, 16, 22, 35, 49, 51, 57	8	21
<i>Vigna sinensis</i>	5, 8, 16, 22, 35, 38, 51, 55, 57, 80	7	24
<i>Wistaria chinensis</i>	5, 16, 31, 35, 55, 57, 71, 75	7	22
<i>Wistaria frutescens</i>	38, 68, 69, 71, 72, 74, 77, 82	2	

* For name of plant, see corresponding number in numerical list of plants.

† Refers to the number of additional plants that have been observed to symbiose with isolate but which have not been included in any group. They are not referred to by number in the numerical list.

chamaecrista, a plant that has been included in the cowpea group, symbiosed with members of five groups, and the isolate from *Lotus corniculatus* symbiosed with members of the following groups: amorpha, bean, cowpea, dalea, locust, lotus, and pea. All twenty-three isolates symbiosed not only with representatives of several groups but also with plants that have not been included in any

group. Since these isolates are not specific for a group, it is evident that, when nodulation is used as a standard of judging, such plants cannot be assigned to any one cross-inoculation group.

Promiscuity of plants with various isolates as related to cross-inoculation groups

If an isolate from a nodule will symbiose with members of several cross-inoculation groups, as shown in table 1, it seems reasonable that a plant might exhibit promiscuity with isolates from nodules of members of several groups. The results obtained from such a combination might depend on the particular strain or strains of the organism that were obtained. In a study of leguminous plants and their associated organisms, Wilson (9) found that *W. chinensis* DC. symbiosed with fourteen of thirty-two isolates that represented several cross-inoculation groups. Also *W. frutescens* Rafin. symbiosed with two of the same thirty-two isolates. These two were from different cross-inoculation groups. Other references to the symbiotic relations between species of *Wistaria* and the rhizobia have not been found in the literature. References to symbiotic promiscuity among the legumes are, however, available. Wilson (10, 11) reviewed the subject, presented data relating to the promiscuity of thirty-seven isolates from *Amorpha fruticosa* DC. with fourteen species of legumes and of one hundred eighty-two isolates from various legumes with two species of *Crotalaria*, suggested that promiscuity is widespread among the legumes, and pointed out that it is closely associated with the degree of self-or cross-pollination of the plants. Some results of exposing plants of various species to such isolates are detailed in table 2.

The nodulation of nine species with isolates from nodules of sixty-one species shows that promiscuity with these diverse isolates is widespread. *Astragalus Nuttalianus* DC. was observed to bear nodules after exposure to isolates from plants that have been included in the following groups: alfalfa, bean, caragana, clover, cowpea, Dalea, and lotus. *Dalea alopecuroides* Willd., a plant comprising one group with a specific organism for that group, bore nodules after exposure to isolates from nodules of plants of eight groups. Also *Desmanthus illinoensis*, a plant that has not been included in any group, developed nodules after exposure to isolates from nodules of plants of seven groups. These findings, therefore, make it possible to assign this plant to each of the seven groups. The promiscuity of other plants with isolates from members of various groups is evident also from the data in table 2.

Incomplete reciprocity of strains with plants and its relation to cross-inoculation groups

If promiscuity exists throughout the Leguminosae between the species of plants and the bacterial strains of the Rhizobia, as indicated in the preceding data, it follows that strains with different serological, morphological, physiological, cultural, and biochemical characters may symbiose with and can be isolated from a certain species or even from an individual plant. Such strains when tested for their symbiobility with numerous species of legumes may exhibit many variations in nodulating performances. Leonard (7) found that four of eleven isolates

from cowpea would not symbiose with soybean, whereas twenty-seven from soybean, representing isolates from four varieties, symbiosed with cowpea. He noted also that in some cases the soybeans were rather poorly nodulated after exposure to the isolates from cowpea, whereas in all cases the isolates from soybean produced almost as good nodulation on cowpea as did the isolates from the cowpea itself. While studying leguminous plants and their associated organisms, Wilson (9) noted several cases of incomplete kinship but cites only one.

TABLE 2

Promiscuity of plants with isolates from various legumes and its relation to the cross-inoculation groups

PLANT USED	ISOLATES FROM PLANTS BELOW SYMBIOSED WITH PLANT USED*	NUMBER OF CROSS-INOCULATION GROUPS REPRESENTED
<i>Astragalus Nuttalianus</i>	9, 10, 11, 12, 15, 16, 24, 25, 31, 35 (7 diverse isolates), 44, 45, 46, 49 (2 of 4 isolates), 54, 58, 67, 74, 80	7
<i>Cassia nictitans</i>	1, 18, 21, 23, 26, 29, 32, 33, 36, 37, 38 (5 of 12 isolates), 43, 45, 50, 54, 64, 80	3
<i>Crotalaria sagittalis</i>	2, 13, 15, 16, 19, 20, 21, 23, 24, 25, 26, 28, 30, 31, 32 (2 isolates), 33, 35, 36, 38 (13 isolates), 42, 44, 50, 53, 59, 61, 67, 73, 78, 80, 82	8
<i>Dalea alopecuroides</i>	5, 15, 20, 29, 31, 34, 38, 46, 54, 59, 61, 63, 78, 82	8
<i>Desmanthus illinoiensis</i>	5, 9, 10, 11, 12, 23 (2 isolates), 27, 28, 30, 31, 32, 33, 34, 35 (7 diverse isolates), 36, 42, 45, 46, 47, 54, 58, 59, 63 (1 of 2 isolates), 76, 78, 80	7
<i>Indigofera suffruticosa</i>	12, 31	2
<i>Lespedeza intermedia</i>	21, 32, 33, 46	2
<i>Lotus corniculatus</i>	2, 15, 31, 38, 42, 46, 51, 53, 57, 58, 61, 62, 63, 73, 80	9
<i>Wistaria frutescens</i> †.....	1, 5 (3 isolates), 9, 11 (6 isolates), 12, 15, 16, 18, 19, 20, 21, 23, 24, 25, 27, 28, 29, 30, 31, 32, 33, 34, 35 (8 diverse isolates), 36, 38 (11 isolates), 40, 44, 45, 46, 47, 49, (4 isolates), 50, 52, 54, 56, 57, 58, 59, 64, 67, 70, 74, 78 (3 isolates), 80, 82	

* For name of plant, see corresponding number in numerical list of plants.

† Plants grown for 50 days.

The isolate from *Amorpha fruticosa* DC. did not symbiose with *Vicia villosa* Roth. whereas the isolate from *V. villosa* symbiosed with both of these species. Sears and Clark (8) found that nine isolates from the garden bean plant failed to effect nodulation on Wood's clover plants, whereas seven isolates from Wood's clover plants symbiosed with the navy and the garden bean plant. These instances do not embody the entire list of references on this subject but merely serve to indicate that such incomplete reciprocal relations do occur and that this fact has been known for two decades.

The meaning of these relations is not known. It relates probably to variations in the strains of the organisms which happen to be in association with the plants, to the heritable background of the plants, to the conditions under which the information was obtained, or to two or more combinations of these. Additional cases of this incomplete reciprocity may serve to aid in the classification of the Rhizobia, to indicate the uselessness of the cross-inoculation groups, or to serve in other capacities.

TABLE 3

Cases of incomplete reciprocity of strains of Rhizobium with leguminous plants

LEGUME USED	ISOLATE FROM THE PLANT LISTED BELOW SYMBIOSED WITH LEGUME USED, BUT ISOLATE FROM LEGUME USED DID NOT SYMBIOSE WITH THE PLANT LISTED BELOW*
<i>Albizzia julibrissin</i>	13, 15, 35, 39, 61, 78, 80
<i>Amphicarpa monoica</i>	2, 61
<i>Cassia chamaecrista</i>	2, 35, 61, 78
<i>Crotalaria spectabilis</i>	2
<i>Dalea alopecuroides</i>	15, 38, 46, 61, 78, 82
<i>Desmodium canadense</i>	15, 35, 61, 63, 73, 78, 80
<i>Glycine max</i>	2, 13, 44, 55
<i>Laburnum vulgare</i>	15
<i>Lespedeza striata</i>	2, 39, 46, 61
<i>Lotus corniculatus</i>	2, 15, 31, 38, 53, 61, 62, 63, 73, 80
<i>Medicago sativa</i>	7, 13, 15, 31, 35, 36, 38, 51, 62, 63, 78, 80
<i>Onobrychis viciaefolia</i>	2, 7, 13, 15, 16, 53, 57, 63, 65, 78, 80, 82
<i>Oxytropis Lambertii</i>	2, 13, 15, 31, 38, 80
<i>Phaseolus vulgaris</i>	2, 7, 13, 15, 16, 31, 35, 44, 46, 63, 78, 80
<i>Robinia Pseudo-Acacia</i>	7, 13, 15, 16, 31, 35, 36, 38, 44, 53, 60, 61, 65, 73, 78, 80, 82
<i>Spartium scoparium</i>	13, 15, 16, 38, 61, 78, 80
<i>Strophostyles helvola</i>	2, 35, 61
<i>Swainsona coronillaefolia</i>	2, 5, 78
<i>Thermopsis caroliniana</i>	2, 13, 15, 35, 36, 44, 46, 53, 59, 61, 63, 80, 81
<i>Trifolium pratense</i>	2, 15, 35, 62, 78
<i>Vicia villosa</i>	44
<i>Vigna sinensis</i>	15, 73
<i>Wistaria chinensis</i>	2, 15, 38, 44, 61, 63, 73

* For name of plant, see corresponding number in numerical list of plants.

As an example of this relationship, in table 3 an isolate from plant number 13, which is *Baptisia australis* R.Br., symbiosed with legume used, *Albizzia julibrissin* Biov. but the isolate from this legume did not symbiose with plant number 13. This indicates the incomplete reciprocal relation of strains of the Rhizobia with leguminous plants.

In table 3 are recorded 146 cases in which there was a lack of complete reciprocal relation. Some of these were between plants within the same cross-inoculation groups and the organisms from these plants. Other cases were between the plants of different groups and their organisms. Still others were between plants unassigned to any group and plants assigned to a group and their organisms.

Only one case was found in which an isolate from a plant symbiosed with *Crotalaria spectabilis* Roth. and in which the isolate from *C. spectabilis* Roth. failed to symbiose with the plant. Similar findings were obtained when *Laburnum vulgare* L. was used. In 17 cases the isolates from different species symbiosed with *Robinia Pseudo-Acacia* L. but the isolate from *R. Pseudo-Acacia* L. did not symbiose with these 17 different species. All other cases came between these extremes.

DISCUSSION

From the nodulating performances of numerous isolates of the root-nodule organism it appears that the cross-inoculation groups are inadequate. The inability to establish boundaries around a certain legume organism or around a definite legume plant indicates that the cross-inoculation groups are inoperative and that from the scientific standpoint they should be abandoned. When a plant assigned to a certain group will bear nodules after exposure to an organism that will symbiose with a plant included in a different group, a flexible boundary if any, exists between the groups. Such proposed boundaries overlap to such an extent in many instances that they seem to vanish. This overlapping from several groups may incorporate plant species and bacterial strains from several of the projected groups. The information recorded in this paper indicates that this does occur, for over 500 cases of overlapping boundaries are recorded.

Since the boundaries between the existing cross-inoculation groups overlap, an isolate from a nodule may belong to any one of several groups. A list of the isolates that symbiose with *Astragalus Nuttalianus* shows that the organisms might be incorporated in any one of the following groups: alfalfa, bean, caragana, clover, cowpea, dalea, and lotus. Also the performance of certain isolates shows that *Wistaria frutescens* might belong to any one of the following groups: alfalfa, amorpha, caragana, clover, cowpea, dalea, locust, lotus, pea, and soybean. It is apparent, therefore, that if either of these two plants had been tested for its ability to symbiose with diverse isolates when the cross-inoculation groups were being projected, some of the groups would never have been suggested. These facts, and similar ones apparent in table 2, make it impossible to say that a certain isolate is specific for any one group or for any one plant. An organism isolated at one time from a plant like *W. frutescens* may possess the salient characters and morphological appearances commonly associated with the organism from alfalfa; at another time, or from another nodule at the same time, the organism may possess the salient characters and morphological appearance of the organism often found associating with caragana or soybean.

If these two species are promiscuous with various isolates, as the data show them to be, it should be suspected that a certain organism from either of them would not symbiose with numerous species such as those from which came the isolates whose organism symbiosed with these two plants. If the plant is restricted in its association with diverse isolates, then it should be suspected that certain organisms from these two promiscuous plants would not symbiose with all plants that are greatly restricted in their symbiotic relations. Such findings

may account for the incomplete reciprocal relations shown in table 3 and indicate the inadequacy of the cross-inoculation groups.

Furthermore, if it is accepted that promiscuity exists as described in this paper, it is evident that a certain isolate can be designated at one time as *Rhizobium phaseoli* and at another time as *R. trifolii* or as something else. From the present information, therefore, the ability of an isolate to effect nodulation on a plant cannot be regarded as one of the prime characters for the differentiation of species of the legume organism. Also the observed incomplete reciprocal relations in one hundred forty-six cases between certain plants and the isolates from these plants, together with the complete reciprocal relations of these same isolates with other plants, are taken to mean that an isolate is not specific when measured in terms of the cross-inoculation groups.

The data presented in this paper are similar to those published by a few other workers. Carroll (3, 4) did not observe nodules on soybean after exposing the plantlets to two isolates from lespedeza, to three from cowpea, to one from Lima bean, or to one from velvet bean, but obtained nodules after exposing the plants to two additional isolates from cowpea. Allen and Allen (1) observed that an organism from a nodule of *Cassia mimosoides* appeared highly adapted to *Phaseolus lunatus*, as evidenced by the formation of numerous nodules, yet an organism also from *C. mimosoides* but from a different locality failed by the same criterion to symbiose with *P. lunatus*.

Some of the results obtained by Conklin (5) bear directly on the overlapping of boundaries between the variously proposed cross-inoculation groups. At least sixty-three bacterial isolates were obtained from nodules of seven species of plants recognized as belonging to the cowpea group, none of which came from the cowpea. Their nodulating performance showed that fifteen isolates would symbiose with soybean, forty-four would not, and the relations of four were questionable.

Aquino and Madamba (2) obtained isolates from nodules of seven species of plants and tested them for their ability to symbiose with all seven species. They found that the isolates from soybean symbiosed with Mungo, lima bean, tapalin, peanut, soybean, Calapogonium, and cowpea. The one isolate from cowpea did not symbiose with soybean but did symbiose with all the other species. Also the isolate from lima bean, from Mungo, and from Calapogonium symbiosed with soybean, a plant supposed to comprise one entire cross-inoculation group with one specific organism.

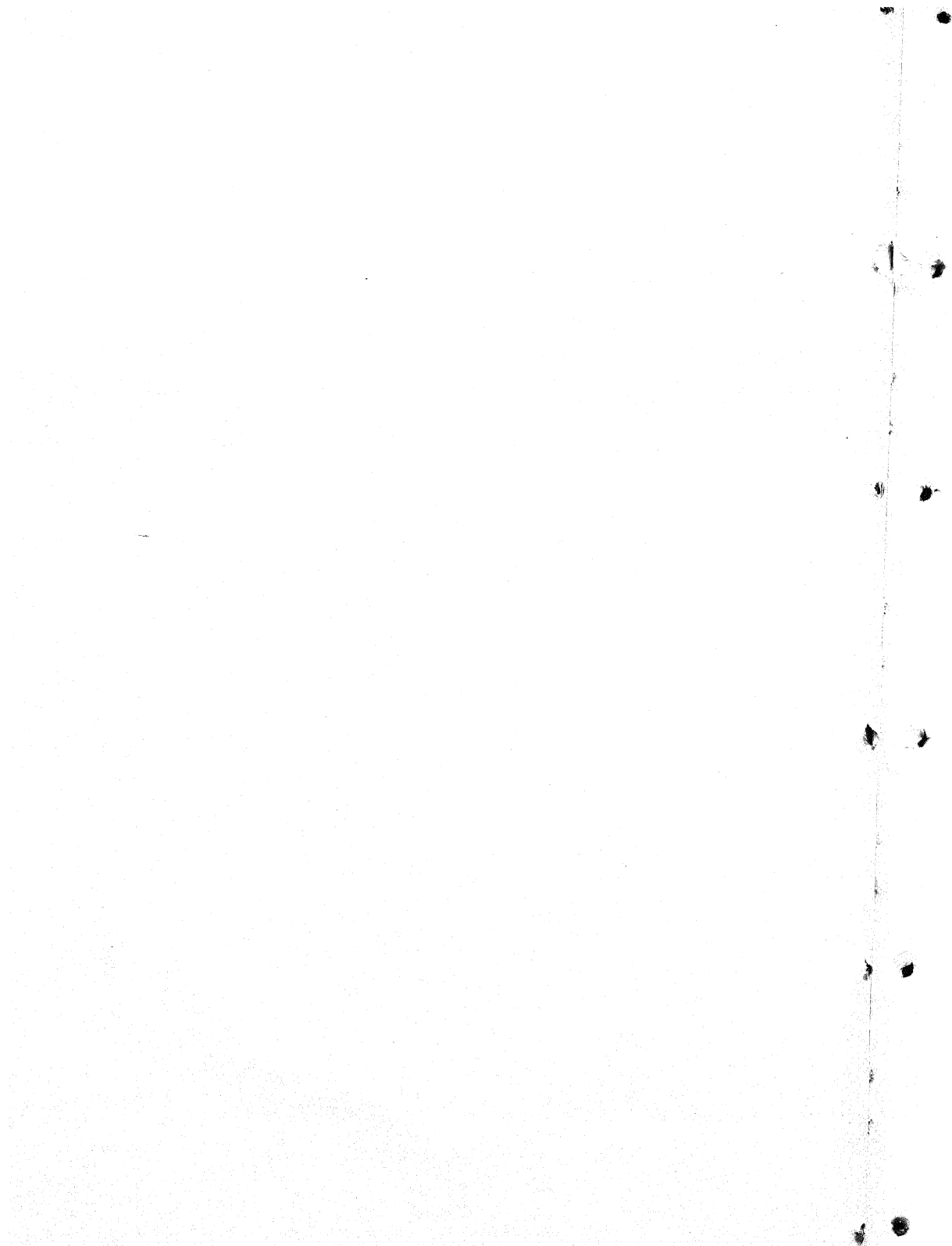
SUMMARY AND CONCLUSIONS

Plants were started from sterilized seed and exposed during their growth to bacterial isolates from the nodules of various leguminous plants. They were grown in soil in glass containers that were plugged with cotton and previously sterilized. The isolates employed were known to symbiose with the plant from which they were obtained, and they comprised one hundred and twenty-five stock cultures. The criterion for placing a plant in any cross-inoculation group was the presence of nodules on the roots of the plants.

The results indicated that the projected boundaries around the twenty-two proposed cross-inoculation groups, which have been built up during the last 56 years, overlap so much that it appeared impossible to assign a plant to one group or to have an organism that was specific for a group. This statement is justified by over five hundred recorded cases in which plants could be assigned to more than one group. It is suggested, therefore, that each of these cases constitutes a reason for abandoning the cross-inoculation groups.

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PHOSPHORUS FIXATION BY THE COARSE AND FINE CLAY FRACTIONS OF KAOLINITIC AND MONTMORILLONITIC CLAYS¹

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Most of the phosphorus fixed by the soil is held by the clay fraction, but the exact manner in which it is held is not known, nor is it known which portion of the clay is responsible for phosphorus fixation. Of the phosphate fixation studies made with clay, some have shown that clay minerals, especially finely ground kaolinite, adsorb large amounts of phosphate, whereas others have shown that free iron and aluminum oxides in clay are primarily responsible for phosphate fixation.

Few studies have been made to show the relative amounts of phosphate fixed by the coarse and fine clay separates. The purpose of the present investigation is to determine the amount of phosphate fixed by the coarse and fine fraction of kaolinitic and montmorillonitic clays, both before and after their free iron and aluminum oxides have been removed, and thus obtain more information on how phosphorus is fixed by clay.

MATERIALS AND METHODS

Both coarse (2-0.2 μ) and fine clay (<0.2 μ) were separated from the C horizons of Orangeburg sandy loam and Susquehanna clay loam. In a previous study² the fine clay of Orangeburg sandy loam was found to consist only of kaolinitic minerals, whereas the fine clay of Susquehanna clay loam was found to consist only of montmorillonitic minerals. The mineral composition of the coarse clay fractions has been determined by x-ray analysis³ as follows:

CLAY MINERAL	SUSQUEHANNA COARSE CLAY	ORANGEBURG COARSE CLAY
	<i>per cent</i>	<i>per cent</i>
Montmorillonite	15 to 20	< 0.2
Kaolinite	10 to 15	60 to 70
Mica	15 to 25	20 to 25
Quartz	50 to 60	10 to 15

Clays were separated from Orangeburg sandy loam and from Susquehanna clay loam by saturating the soils with sodium using *N* NaOH, dispersing in a mechanical stirrer, shaking in an 18-liter carboy, and siphoning adequate amounts

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² Coleman, R. The mineral composition of the colloidal fraction of five Coastal Plain soils. 1941. (Doctoral Dissertation, University of Wisconsin, Madison.)

³ The author is indebted to M. L. Jackson, J. B. Pitner, and N. N. Hellman, soils department, University of Wisconsin, Madison, for making the x-ray analyses.

after the material ($>2\mu$) in diameter had settled according to Stokes' law. The fine clay ($<0.2\mu$) was separated from the coarse clay ($2-0.2\mu$) by the centrifuge-decantation method described by Truog *et al.* (10). After the clays were made to a suitable volume and their concentrations determined, 1-gm. aliquots were placed in 100-ml. centrifuge tubes. The clays were hydrogen-saturated by washing with four 50-ml. portions of dilute HCl adjusted to pH 2, and were ammonium-saturated by washing with four 50-ml. portions of *N* ammonium acetate. In either case the excess acid or salt was removed by washing with methyl alcohol until all traces of chlorides or ammonia were removed.

The phosphate solution used for the fixation studies consisted of a H_3PO_4 solution, containing 1000 mgm. of PO_4 per liter, which had been adjusted to pH 3.0, 7.0, or 9.5 by dilute NH_4OH . The clays were dispersed in 50 ml. of the phosphate solution (containing 50 mgm. PO_4) and shaken for 24 hours on a rotary shaker. After the pH of the clay-phosphate solution was determined, the clays were flocculated with about 0.5 gm. of NH_4Cl and centrifuged. The phosphated clays were washed three times with 50 ml. of 70 per cent methyl alcohol, and all of the phosphate removed from the clays was determined. The phosphate not removed was considered to be fixed.

Phosphorus was determined by the Fiske and Subarrow method as described by Parker and Fudge (8), with the following modifications: Before being analyzed, the solutions containing the phosphate were made up to 250 ml., of which 10 ml. was used for the determination. After the color had been developed and the solution had been made up to 500 ml., the phosphorus concentration was determined at the end of 5 minutes by using an Evelyn photoelectric colorimeter. Along with every phosphorus determination, both a blank, containing only the reagents, and a known, containing the same amount of PO_4 as that applied to the clay, were analyzed. All determinations were made in duplicate.

Both coarse and fine clay minerals are coated with considerable amounts of free iron and aluminum oxides. In order to determine the adsorptive capacity of the clay minerals and the free iron and aluminum oxides, phosphate-fixation studies were made on the clays with the free iron and aluminum oxides present and also on the clay minerals after the free iron and aluminum oxides were removed. The free iron and aluminum oxides were removed from the clay minerals by the method of Truog *et al.* (10), with the following modifications: 1 gm. of clay, instead of 10 gm. of soil, was used; and the clay minerals were washed with HCl (adjusted to pH 2) until all of the free iron and aluminum oxides were removed, as shown by the potassium ferrocyanide test. Previous studies (2) have shown that such a removal of the free iron and aluminum oxides does not destroy the crystal lattice of the clay minerals.

RESULTS

Phosphate fixation by coarse and fine clays

The amount of phosphate fixed by the hydrogen- and ammonium-saturated coarse clays at different reactions is pictured graphically in figure 1. In each case the coarse clays fixed considerable amounts of PO_4 . The amount fixed was

dependent, however, upon the reaction of the phosphate solution as well as the type of exchangeable cation held by the coarse clay. The H-clays fixed more PO_4 than similarly treated NH_4 -clays, and in every case the coarse clays fixed more PO_4 from acid phosphate solutions than from neutral or alkaline phosphate solutions.

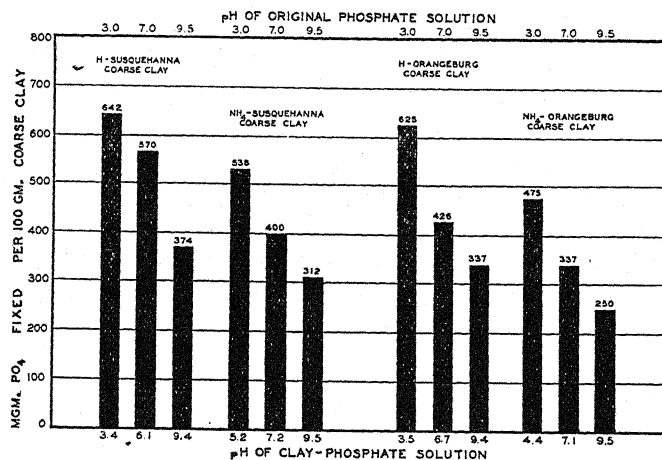


FIG. 1. PHOSPHATE FIXED BY SUSQUEHANNA (MONTMORILLONITIC) AND ORANGEBURG (KAOLINITIC) COARSE CLAYS

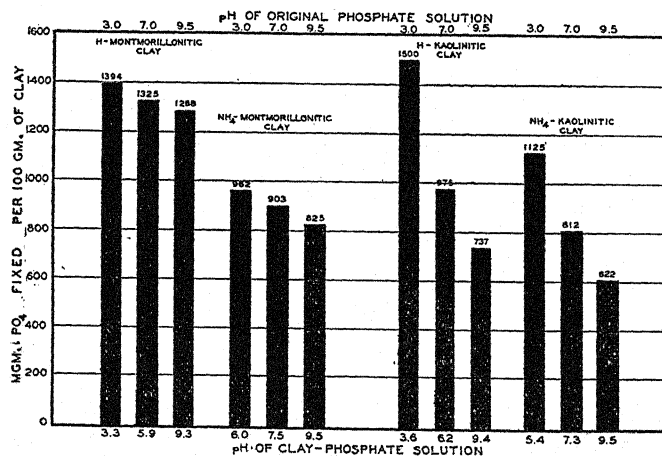


FIG. 2. PHOSPHATE FIXED BY MONTMORILLONITIC AND KAOLINITIC FINE CLAYS

The fixation of phosphate by montmorillonitic (Susquehanna) and kaolinitic (Orangeburg) fine clays has been discussed in detail in a previous study (2), but in order to compare their fixation of phosphate with that of the coarse clays from which they were separated, the results with fine clays are pictured graphically in figure 2.

A comparison of figures 1 and 2 shows that, in most cases, the coarse clay fixed about one half as much phosphate as the fine clay. The fixation by the coarse clays, however, was influenced by reaction and the exchangeable cation in a manner similar to the fine clays from which they were separated. In every case the H-clays fixed more PO_4 than similarly treated NH_4 -clays, and in each case more PO_4 was fixed at an acid than at a neutral or alkaline reaction. The fact that the clays fix more phosphate at the lower pH suggests that either the clay minerals adsorb more PO_4 or that the iron and aluminum oxides are more active in fixing PO_4 at the lower pH.

Phosphate fixation by coarse and fine clay minerals after removal of free iron and aluminum oxides

After the free iron and aluminum oxides were removed from the coarse clays, the clay minerals were unable to fix PO_4 regardless of the type of exchangeable

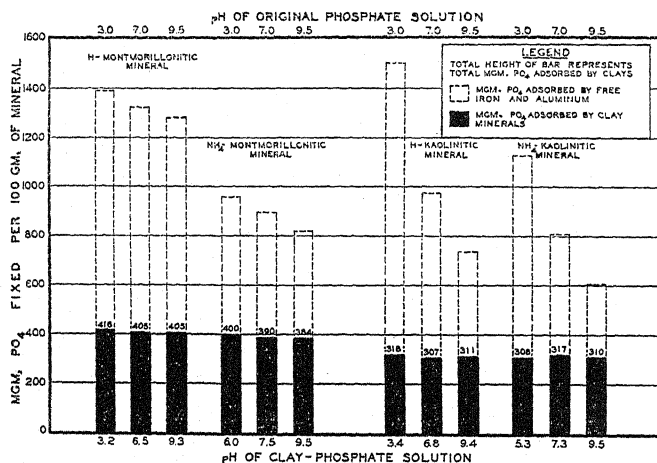


FIG. 3. PHOSPHATE FIXED BY H- AND NH_4 -MONTMORILLONITIC AND KAOLINITIC MINERALS

cation or the reaction of the phosphate solution. These results show conclusively that the coarse clay minerals, even though they contain appreciable amounts of kaolinite or montmorillonite, cannot fix phosphate, and that all of the phosphate fixed by coarse clay is due to its free iron and aluminum oxides. Therefore, the greater fixation of PO_4 by coarse clay under acid conditions must be due to the greater activity of the free iron and aluminum oxides at a low pH.

The amount of phosphate fixed by the fine clay minerals after the free iron and aluminum oxides were removed is shown in figure 3. After the free iron and aluminum oxides were removed, both Susquehanna (montmorillonitic) and Orangeburg (kaolinitic) fine clays lost most of their ability to fix phosphate, which shows that the free iron and aluminum oxides in fine clay are largely responsible for phosphate fixation. Even after the free iron and aluminum oxides were removed from the fine clay, however, both montmorillonitic and kaolinitic clay minerals fixed appreciable amounts of phosphate. The studies with fine and

coarse clay show that the montmorillonitic and kaolinitic minerals that occur in fine clay are capable of fixing phosphate, whereas the kaolinite, montmorillonite, and other minerals that occur in coarse clay are unable to fix phosphate. In both coarse and fine clay, phosphate fixation is largely due to the free iron and aluminum oxides and not to the clay minerals.

The similarity between the manner in which phosphorus is fixed by the coarse and fine clay fractions before the free iron and aluminum oxides are removed, and the fact that, in coarse clay, phosphate fixation is due altogether to the free iron and aluminum oxides, offer further evidence to support the belief that phosphate fixation by either coarse or fine clay is determined largely by the activity of the free iron and aluminum oxides.

The total amount of free iron and aluminum oxides in the coarse and fine clays is shown in table 1. There is a close correlation between the amount of free iron and aluminum oxides in the clays and the amount of phosphate fixed, especially under acid conditions. For example, Susquehanna coarse clay containing 74.3 mgm. of free R_2O_3 adsorbed 6.42 mgm. PO_4 per gm. at pH 3, and Susquehanna

TABLE 1
Amounts of free iron and aluminum oxides in clays

CLAY	PO ₄ FIXED BY H-CLAYS IN pH 3.0 PHOSPHATE SOLUTION	FREE R ₂ O ₃ IN CLAY	FREE Fe ₂ O ₃ IN CLAY	FREE Al ₂ O ₃ IN CLAY
	mgm./gm.	mgm./gm.	mgm./gm.	mgm./gm.
Susquehanna coarse clay	6.42	74.3	59.2	15.1
Susquehanna (montmorillonitic) fine clay.....	13.80	140.8	87.0	53.8
Orangeburg coarse clay.....	6.25	63.6	43.6	20.0
Orangeburg (kaolinitic) fine clay.....	15.0	157.5	110.0	47.5

fine clay containing 140.8 mgm. of free R_2O_3 adsorbed 13.80 mgm. PO_4 per gm. The coarse clays, containing about one half as much free iron and aluminum oxides, fix about one half as much PO_4 as the fine clays.

DISCUSSION

Although it is known that the clay fraction of the soil is responsible for phosphorus fixation, it is not definitely known which constituent of clay has the greatest ability to fix phosphate. Murphy (7) and Stout (9) contend that the type of clay mineral largely determines the amount of phosphate fixed by the soil. Ford (3) and Heck (4) believe that hydrated iron and aluminum oxides in the soil are primarily responsible for phosphate fixation. From their investigations, Metzger (6) and Chandler (1) concluded that phosphorus fixation in the soil is largely due to the free iron and aluminum. Murphy (7) found that since only small amounts of soluble iron and aluminum occur in soils, it is impossible for iron and aluminum to fix large amounts of phosphate. Some investigations have shown, however, that iron and aluminum need not be in solution in order to re-

act with phosphate. Recently Kelly and Midgley (5) have found that both the clay mineral and the free iron and aluminum oxides fix phosphate by anion exchange.

The results of the present investigation show that in both coarse and fine clay fractions the free iron and aluminum oxides are largely responsible for phosphorus fixation. In the fine clay fraction most of the phosphate is fixed by these oxides, and in the coarse clay fraction all of the phosphate is fixed by them.

Although previous investigations have shown that the maximum amount of PO_4 is fixed under acid conditions, the exact reason for this has not been definitely established. Chandler (1) believed that more PO_4 was fixed under acid conditions because of its greater precipitation by iron and aluminum. Stout (9) also found that clays fix more phosphate at a low pH, but he believed that this was due to the greater adsorbing power of certain clay minerals under acid conditions. The results of the present investigation show convincingly that the greater fixation of PO_4 at a low pH is due to the greater activity of the free iron and aluminum oxides rather than to the greater adsorption by the clay minerals, for in both coarse and fine clays the amount of PO_4 fixed is influenced by reaction only as long as the free iron and aluminum oxides are present. After these free oxides are removed, the amount of PO_4 fixed by the clay minerals is influenced neither by the reaction of PO_4 solution nor by the type of exchangeable cation. The coarse clay fraction, containing about one half as much free iron and aluminum oxides as the fine clay fraction, fixes about one half as much phosphate, and the close correlation between the amount of PO_4 fixed and the amount of these free oxides present suggests that phosphate fixation by the clay is largely determined by the amount and activity of the free iron and aluminum oxides in clay.

Most phosphate fixation studies have been made with the clay fraction of pure clay minerals. It is believed that phosphate fixation, as it occurs in the soil, has been more nearly duplicated by the use of clays with a known mineral composition in the present study than in previous studies where pure clay minerals were used.

SUMMARY

The coarse and fine clay fractions of Susquehanna clay loam and of Orangeburg sandy loam were used to study phosphorus fixation by montmorillonitic and kaolinitic clays. Phosphorus fixation studies were made with hydrogen- and ammonium-saturated clays at different reactions both before and after the free iron and aluminum oxides were removed.

All of the phosphorus held by the coarse clay and most of the phosphorus held by the fine clay are fixed by the free iron and aluminum oxides. Kaolinite and montmorillonite in the fine clay fix appreciable amounts of PO_4 , but the kaolinite, montmorillonite, quartz, and mica in the coarse clay minerals are unable to fix phosphate.

Phosphorus fixation by both coarse and fine clays is influenced by reaction and exchangeable cations only as long as the free iron and aluminum oxides are present, which shows that the activity of these free oxides determines the amount of PO_4 fixed by the clay.

The coarse clays, containing about one half as much free iron and aluminum oxides as fine clays, fix about one half as much PO_4 .

The amount of PO_4 fixed by clay is influenced not so much by the type of clay mineral as by the amount and activity of the free iron and aluminum oxides contained.

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SOIL COLLOIDS: IV. DISTRIBUTION AND AVAILABILITY OF PHOSPHORUS¹

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Previous papers³ presented some results obtained by applying Tyulin's method⁴ for the fractionation of soil colloids to the study of a number of Canadian soils. Briefly, the method consisted of the separation of the soil colloids into group 1 and group 2, the latter being obtained as two subgroups. Group 1 was made up of colloids which, when saturated with sodium ions, were dispersed in distilled water. Group 2a consisted of the colloids which, after removal of group 1, were dispersed in 0.004 *N* NaOH solution. After group 2a was removed, the soil was treated several times with 0.01 *N* HCl, and group 2b was then dispersed in weak alkali. The groups so separated were further treated so as to give humate fractions representing both loosely bound organic matter and organic matter more firmly attached to the colloids.

The results previously presented indicated that the amounts of group 1 colloids showed considerable variation, from 1.1 to 19.3 per cent for seven soils of medium texture. There was less variation in the amounts of groups 2a and 2b. There was also an apparent relationship between the amount of group 1 colloids and the productivity of the soil as measured by yields of barley (two seasons) and of clover (one season) obtained in greenhouse studies over a period of 3 years. This pointed to the importance of the group 1 colloids in soil fertility.

DISTRIBUTION OF PHOSPHORUS AMONG COLLOID GROUPS

One of the objects in carrying out this investigation was to study the relationship between the distribution of phosphorus among the different groups and its availability to plants, and to see whether the fixation of phosphorus applied to the soil in the form of a fertilizer was associated with its distribution in the colloidal fractions. The amount of phosphorus was therefore determined in each group, in the residue after the removal of the groups, and in the HCl solution used to treat the soil between the separation of group 2a and that of group 2b. The results so obtained, expressed as percentages of the total soil phosphorus, are given in table 1.

¹ Scientific contribution No. 110 from the Division of Chemistry, Science Service, Dominion of Canada Department of Agriculture.

² Associate chemist and agricultural assistants, Division of Chemistry, Science Service, Central Experimental Farm, Ottawa, Canada.

³ Atkinson, H. J., and Turner, R. C. 1944 Soil colloids: II. Separation by peptization. *Soil Sci.* 57: 233-240.

Atkinson, H. J., Turner, R. C., and Leahey, A. 1944 Soil colloids: III. Relationship to soil fertility. *Soil Sci.* 57: 243-246.

⁴ Tyulin, A. Th. 1938 The composition and structure of soil organo-mineral gels and soil fertility. *Soil Sci.* 45: 343-357.

The distribution of phosphorus showed considerable variation with the different soils. The amounts found in group 1 varied from 8.6 per cent of the total for the Sawyerville soil to 47.7 per cent of the total in the case of Lacombe 512. In general, the percentage of the soil phosphorus found in group 1 was of the same order as the total quantity of group 1 colloids in the soil, except in Lacombe C, which gave the second highest quantity of this group but ranked fourth in the percentage of the phosphorus found in the group. There was a distinct difference between the two Lacombe samples. The Lacombe 512 sample had a greater fraction of its phosphorus in group 1 than in group 2a, whereas the Lacombe C sample had the greater amount in group 2a. In the Sawyerville sample, the largest fraction was in group 2a, and in that from Ottawa, the largest fraction was found in group 2b. The amount of phosphorus that came out in the HCl treatment of the soil following the removal of group 2a was in most cases very small (less than 0.5 per cent) except in the case of the Ottawa sample, where it amounted to 2.5 per cent.

TABLE 1

Distribution of phosphorus in the different groups of colloids in selected Canadian soils
As percentages of the total phosphorus of the soil

SOIL	GROUP 1	GROUP 2a	HCl TREATMENT	GROUP 2b	RESIDUE	PERCENTAGE ACCOUNTED FOR
Ottawa.....	15.1	13.8	2.5	40.6	21.8	93.8
Nappan.....	29.1	34.1				
Lacombe C.....	32.1	41.5	0.4	9.9	12.6	96.5
Lacombe 512.....	47.7	33.7	0.3	15.9	13.9	111.5
Sawyerville.....	8.6	48.6				
Breton.....	32.4	27.8	0.2	23.2	23.0	106.6
Scott.....	46.4	27.9	0.2	13.4	12.5	100.4

AVAILABILITY OF PHOSPHORUS IN GROUP 1

As mentioned in the preceding paper of this series, an apparent relationship was found between the amounts of group 1 colloids and the yields obtained from the soils in greenhouse studies. It might therefore be expected that the phosphorus of the colloids of this group would be more readily available than that of the other groups, and, if such were the case, some relationship might be shown between the phosphorus found in group 1 colloids and that taken up by the plants in the greenhouse. Since the amount of phosphorus in the plants (exclusive of the roots) had been determined, it was possible to make the desired comparison. In table 2 are presented figures showing the total soil phosphorus (expressed as percentage of P_2O_5), the phosphorus found in group 1 colloids (as percentage of the total soil phosphorus), and the phosphorus taken up by the plants (in milligrams of P_2O_5 per pot) over a period of 3 years, by barley in 1940-41 and in 1941-42, and by clover in 1942-43.

It can be readily seen that there was no relationship between total soil phos-

phorus and that fraction that came out in group 1, or between total soil phosphorus and that taken up by the plants. On the other hand, there does appear to be some relationship between the amount of phosphorus found in the barley and clover and the percentage of the soil phosphorus that was found in group 1. With the barley in 1940-41, the phosphorus content of the Lacombe C sample was slightly out of line, and, for the same soil, it was very much out of line in 1941-42. When clover was grown in 1942-43, however, the amounts of phosphorus found in the crop showed a direct relationship with the amounts of phosphorus in the first group of colloids.

COMPARISON OF TREATED AND UNTREATED SOILS

From three of the seven locations from which the foregoing samples were taken, corresponding samples were available from areas which had been treated with phosphatic fertilizer for a sufficiently long time to increase appreciably the total phosphorus of the soil. The different groups of colloids were separated from

TABLE 2

Relationship between the phosphorus in group 1 colloids and that taken up by plants in the greenhouse

SOIL	TOTAL SOIL PHOSPHORUS (AS PER CENT P_2O_5)	PHOSPHORUS IN GROUP 1 (AS PER CENT OF TOTAL)	PHOSPHORUS TAKEN UP BY PLANTS (MG. P_2O_5 PER POT)		
			Barley 1940-41	Barley 1941-42	Clover 1942-43
Lacombe 512.....	0.210	47.7	48.5	81.5	86.1
Scott.....	0.137	46.3	43.9	32.7	64.1
Breton.....	0.124	32.4	29.1	23.1	57.7
Lacombe C.....	0.215	32.1	36.4	55.2	53.3
Nappan.....	0.055	29.1	20.4	15.8	23.6
Ottawa.....	0.160	15.1	11.7	15.6	16.0
Sawyer ville.....	0.119	8.6	5.7	4.8	

these samples, and phosphorus was determined in each group, so that a comparison could be made with the results from the untreated samples. Since the treated soils were not used in the greenhouse work, the availability of the soil phosphorus to plants was determined by the Neubauer method for both treated and untreated samples. The results obtained for the distribution of the phosphorus among the groups (expressed as milligrams of P_2O_5 from 50 gm. of soil), and for the available phosphorus (as parts per million P_2O_5) are presented in table 3.

The figures for the three untreated soils reveal that the Neubauer results showed a variation similar to that for the phosphorus in group 1. Thus the Ottawa untreated soil with 12.1 mgm. P_2O_5 in group 1 (equivalent to about 15 per cent of the total phosphorus), contained the least available phosphorus (7.6 p.p.m. P_2O_5). The Lacombe untreated sample, with 50.3 mgm. P_2O_5 in group 1 (approximately 48 per cent of the total) had the largest amount of available phosphorus (74.4 p.p.m. P_2O_5). The Breton untreated sample gave intermediate values, 20.0 mgm. P_2O_5 in group 1 (about 32 per cent of the total), and a Neubauer value of 21.3 p.p.m. P_2O_5 .

A comparison of the results for treated and untreated samples shows that, in all cases, more phosphorus came out in group 1 of the treated samples, less phosphorus appeared in group 2a of the treated samples (though the difference in the case of the Breton samples was negligible), and slightly more phosphorus was found in group 2b of the treated soils in two cases (Lacombe and Breton). With the Ottawa sample only, considerably more phosphorus appeared in the HCl treatment and in the residue of the treated soil. The Neubauer results on the treated samples were greater than on the untreated samples in the case of the Lacombe and Breton soils (by 43.5 and 36.2 p.p.m. P_2O_5 respectively), but there was only a very slight difference (2.2 p.p.m. P_2O_5) in these values between the two Ottawa samples.

Since the total amounts of the phosphorus in the groups and in the residue do not in every case exactly equal the phosphorus content of the original soil, differences of a few milligrams may not be important in making comparisons. It appears, however, that the increase in total soil phosphorus due to applied phos-

TABLE 3

Distribution of phosphorus in the different groups of colloids of treated and untreated soils
As milligrams of P_2O_5 from 50 gm. of soil

SOIL	GROUP 1	GROUP 2a	HCl TREAT- MENT	GROUP 2b	RESIDUE	TOTAL IN GROUPS	TOTAL IN SOIL	PERCENT- AGE AC- COUNTED FOR	AVAIL- ABLE P_2O_5 (NEU- BAUER)
									<i>p.p.m.</i>
Lacombe 512, untreated..	50.3	35.5	0.3	16.8	14.6	117.5	105.3	111.6	74.4
Lacombe 512, treated....	59.7	28.4	0.4	19.2	14.3	122.0	112.2	108.7	117.9
Breton, untreated.....	20.0	17.2	0.2	14.4	14.2	66.0	61.8	106.8	21.3
Breton, treated.....	34.7	16.7	0.4	18.8	15.0	85.6	76.7	111.6	57.5
Ottawa, untreated.....	12.1	11.1	2.0	32.6	17.5	75.3	80.1	94.0	7.6
Ottawa, treated.....	16.2	7.0	11.9	30.9	43.0	109.0	108.7	100.3	9.8

phatic fertilizers in the case of the Lacombe and Breton samples was accompanied by a similar increase in the phosphorus of group 1 colloids. This increase was reflected in a substantial increase in the available phosphorus as measured by the Neubauer method. On the other hand, the increase in total soil phosphorus in the Ottawa treated sample was paralleled by an increase in the phosphorus content of the residue left after the removal of the groups, and the increase in the phosphorus of group 1 was only slight. This distribution of the phosphorus was reflected in its availability (as shown by the Neubauer determination), which was only very slightly increased in the treated sample.

One other difference between the Ottawa samples and those from Lacombe and Breton was found in the reactions. The pH values as determined on the original samples were as follows:

Ottawa..... untreated, pH 7.3; treated, pH 7.6.
Lacombe 512..... untreated, pH 6.5; treated, pH 6.5.
Breton..... untreated, pH 6.5; treated, pH 6.6.

The Ottawa samples are slightly alkaline in reaction, the others, slightly acid. It is possible that this difference may have caused the applied phosphorus to be held in a different manner in the Ottawa soil from that in the other two. Nevertheless, it is important that such a difference was shown in the distribution of the phosphorus among the groups and in its availability as measured by the Neubauer method.

DISCUSSION

The investigation of problems connected with the study of soil colloids by means of Tyulin's method of fractionation has produced in this laboratory some rather interesting results, not the least interesting of which have been those on the distribution of soil phosphorus and its availability to plants, as presented in this paper. The availability of soil phosphorus is usually measured by various methods of chemical extraction, supplemented by other methods such as that of Neubauer. Just what fraction of the soil phosphorus is thus measured is rather obscure. The results presented herewith have indicated that the phosphorus of the group 1 colloids is important from the point of view of its availability to plants. Both greenhouse results and Neubauer tests have given evidence pointing in this direction. It is true that only a few soils of medium texture have as yet been examined, and no attempt is being made at present to draw too general conclusions. Nevertheless, it is believed that a new approach has been made to a rather difficult problem. If it can be shown that the phosphorus of group 1 colloids is most readily obtained by plants, whereas that found, for example, in group 2b or in the residue, cannot be easily utilized, then an important step will have been made. These few results are therefore presented at this time in the hope that they will contribute toward the advancement of our knowledge of the problems of phosphorus fixation and utilization.

SUMMARY

A study of the distribution of phosphorus among the groups of soil colloids separated by Tyulin's method of fractionation has shown that this varied considerably among a number of Canadian soils. The amount of phosphorus in the colloids of group 1 was found to vary from 8.6 to 47.7 per cent of the total phosphorus of the soil for the seven samples examined. The largest fraction was not always found in the same group with the different soils but was sometimes in group 1, sometimes in group 2a, and, in one case, in group 2b. There appeared to be no relationship between the total soil phosphorus and the phosphorus uptake by plants, or between total soil phosphorus and that part of the total found in group 1. There was, however, an apparent relationship between the phosphorus taken up by the plants in the greenhouse (results of 3 years' work) and the percentage of the total soil phosphorus found in group 1 colloids.

Samples of untreated soils from three locations were compared with corresponding samples from adjacent areas where the total phosphorus had been appreciably increased by applications of phosphatic fertilizers over a period of years. For the three untreated soils, a relationship was indicated between the

phosphorus of group 1 colloids and the available phosphorus as determined by the Neubauer method. With the treated samples, it was shown that the added phosphorus appeared in group 1 colloids in two cases but was found in the residue after separation of the groups in the third. Where the added phosphorus appeared in group 1, the available phosphorus as determined by the Neubauer method was considerably greater. On the other hand, where the added phosphorus was found to be in the residue, there was no appreciable increase in the Neubauer value. All the results have thus indicated the importance of the phosphorus of the group 1 colloids from the point of view of the availability of soil phosphorus to plants.

BOOKS

Asia's Lands and Peoples. By GEORGE B. CRESSEY. McGraw-Hill Book Company, Inc., New York, 1944. Pp. 608. Price, \$4.50.

This is the first edition of a "geography of one-third of the earth and two-thirds of its people." The subject is of such immensity that the author is compelled to deal with only the more general phases of it, but he has done an exceptionally good piece of work nevertheless. Thus the human heritage, history, political patterns, population problems, communications, geological foundations, river patterns, surface configuration, climate, natural vegetation, soils, mineral resources, geographic forecast, agricultural landscape, land use, and agricultural regions are discussed for China as a whole, and special attention is paid to other supplementary phases of the geography of the several regions of that great nation. Similarly, Japan, the Soviet Union, Turkey, Syria, Arabia, India, Burma, Indo China, the Netherlands Indies, and the Philippines, together with the smaller lands lying in between, are all considered. The book is especially well illustrated and is an attractive volume for study, for pick-up reading, and for reference.

The Chemistry of Synthetic Substances. By EMIL DREHER. Philosophical Library, New York, 1943. Pp. 102. Price, \$3.

This small volume is an introduction to the macromolecular organic compounds which are assuming ever-increasing importance in the field of industrial synthesis. The several chapters deal with principles of polymerization processes, chemistry of the compounds, types of products, influence of constitution and substituents on capacity for polymerization, principles of polycondensation processes, and solubility of high-molecular film-forming substances. The book is designed to aid in the simplification of the manufacture of lacs and paints.

Food. By FRANK A. PEARSON AND DON PAARLBERG. Alfred A. Knopf, New York City, 1944. Pp. 239, figs. 4. Price, \$2.75.

The authors have undertaken to speak for "rugged individualists," "economic royalists," the "one-to-fourteen-caret liberals," and the "heretics and unbelievers" in the "new doctrine of planned economy." The book contains a good bit of vinegar, and some spinach, which the senior author, a Scotchman, eats, and the junior author doesn't. Among the conclusions reached are these: "If food is to write the peace, it will have to write for many people. The only way our food supply can be written for many people is in terms of wheat, beans, and potatoes, rather than milk, eggs, and meat." The book can be read by the rapid reader in an hour, but it bears studying for several evenings. All the authorities on food, which the authors say include the farmer, the middleman, the housewife, and the consumer, will find this book highly interesting and instructive.

Handbook of Chemistry. Fifth edition. Compiled and edited by NORBERT ADOLPH LANGE. Handbook Publishers, Inc., Sandusky, Ohio, 1944. Pp. 1777. Price, \$6.

This is the most comprehensive chemical handbook that has yet been compiled. It begins with first-aid measures for accidents and with antidotes for poisons and ends with the three-hundred-year calendar. It contains a two-part mathematical appendix, the first of which has to do with formulas and theorems from elementary mathematics, and the second with logarithmic and other tables and with symbols and abbreviations, including the Greek alphabet. One of the most satisfying features of the book is its very complete index of 28 pages, with about 100 items on each page. The new tables in this edition include Deming's periodic chart of the elements, flammable liquids, flame temperatures, plastics, fluorescence of chemicals, minerals and gems, and water for industrial use. Some 13 other tables have been considerably extended or entirely rewritten. Every laboratory will want to have a copy of this volume at hand for ready reference.

Inorganic Plant Nutrition. By D. R. HOAGLAND. Chronica Botanica Company, Waltham, Massachusetts, 1944. Pp. 226, figs. 44, plates, 28. Price, \$4.

This book comprises the Prather lectures given by the author at Harvard University. The topics of these lectures are: a survey of problems of plant nutrition, micronutrient chemical elements and plant growth, absorption and accumulation of salts by plant cells, upward movement and distribution of inorganic solutes in the plant, growth of plants in artificial media in relation to the study of plant nutrition, biological problems associated with salt absorption, and aspects of the potassium nutrition of plants as illustrating problems of the system soil-plant-atmosphere. This is a thought-stimulating presentation which every scientific worker in the field of soil-plant relationships will want to read and study.

Natural Principles of Land Use. By EDWARD H. GRAHAM. Oxford University Press, New York, 1944. Pp. 274, plates, 32. Price, \$3.50.

This book is written from the point of view of the biologist who feels that "biological concepts can contribute importantly to the wise use and management of land." Thus the author begins with a discussion of ecology, the natural distribution of plants and animals, the communities of living things, plant succession, and plant indicators, and then proceeds to a consideration of the land itself, the farms, forests, range, wildlife, and waters, with an additional chapter on control of predatory forms of life and another on land in relation to human welfare. The author's point is that any device for land use that fails to take the natural biological agencies into consideration is doomed to failure, but that one that takes advantage of these agencies holds great promise of success.

Palestine, Land of Promise. By WALTER CLAY LOWDERMILK. Harper and Brothers, New York City, 1944. Pp. 236, illus. 16. Price, \$2.50.

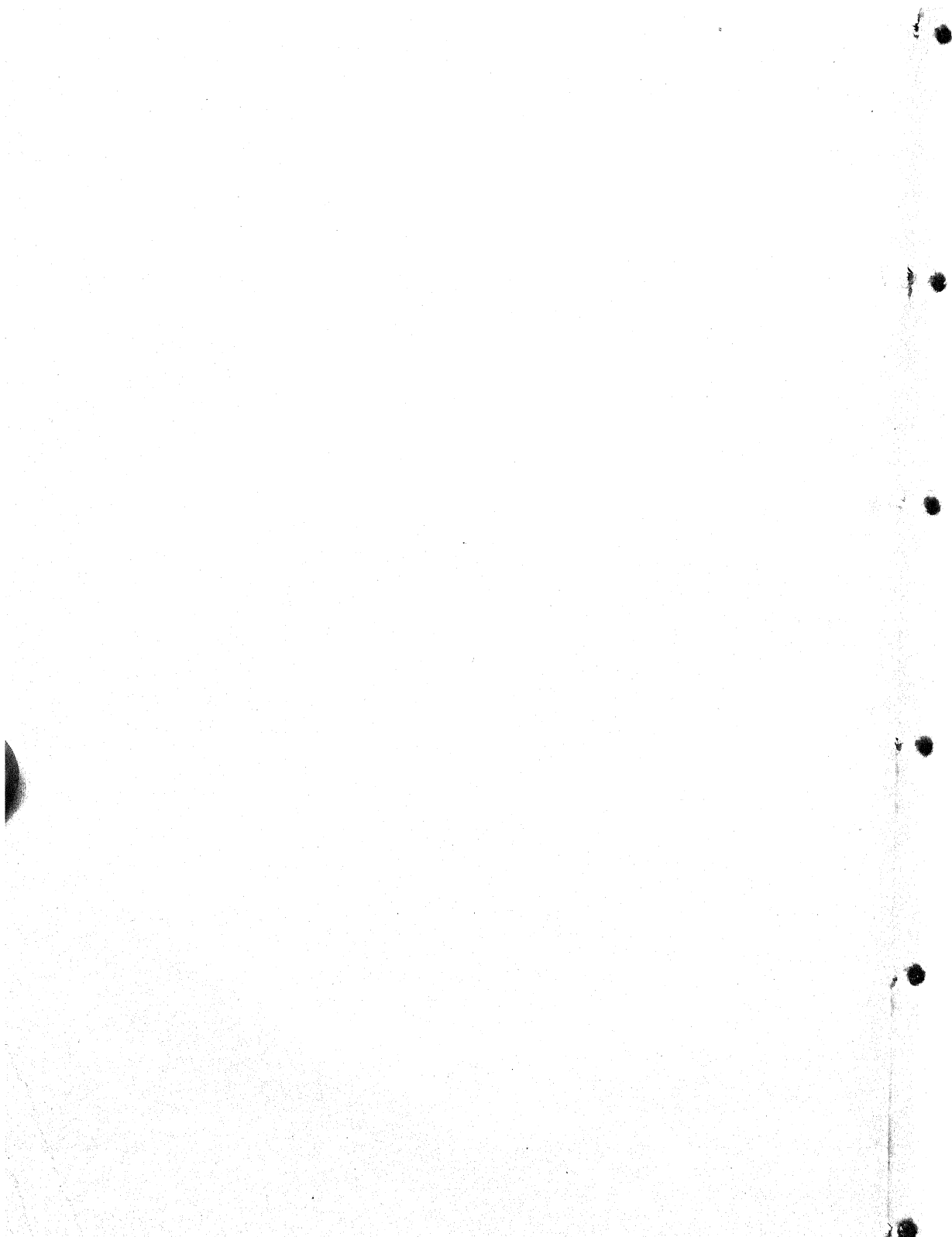
The book is written from the point of view of the soil conservationist who saw

"thousands of goat paths, like festoons of dismal slopes, revealing long abuse and extensive overgrazing." But "along with the records of decay in the Holy Land" he "found a thorough-going effort to restore the ancient fertility of the long-neglected soil"—the most remarkable he had ever seen. The number of Jews in Palestine rose from 50,000 in 1918 to over 550,000 in 1943, and now constitutes over one third of the total, of which 900,000 are Moslem Arabs and 125,000 Christians. Assigned the task by Henry A. Wallace, then Secretary of the Department of Agriculture, Dr. Lowdermilk made a thorough analysis of the agricultural situation in Palestine, of which this book constitutes a report. He concludes: "If the forces of reclamation and progress Jewish settlers have introduced are permitted to continue, Palestine may well be the haven that will transform the other lands of the Near East. Once the great undeveloped resources of these countries are properly exploited, twenty to thirty million people may live decent and prosperous lives where a few million now struggle for a bare existence." Every technical agriculturist in America should read this book and ponder over what it reveals.

Semimicro Quantitative Organic Analysis. By E. P. CLARK. Academic Press, Inc., New York City, 1943. Pp. 135, figs. 31. Price, \$2.50.

This book is an outgrowth of research in the chemistry of natural products. The approach is half way between the ordinary quantitative procedures and the microtechniques. The methods include those for carbon, nitrogen, halogens, sulfur, phosphorus, the methoxyl, ethoxyl, and acetyl groups, neutralization equivalents, molecular weights, and volatile fatty acids. Tables on gravimetric factors, barometric corrections for temperature, atomic and molecular weights and formulas, and logarithms are appended. This is a very useful reference book for workers in this field of chemistry.

THE EDITORS.



THREE DECADES WITH SOIL FUNGI¹

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To Dr. Charles Thom, recently retired from his position as Microbiologist in the Bureau of Plant Industry, Soils, and Agricultural Engineering, U. S. Department of Agriculture, who has contributed in a large measure to the development of our knowledge of the fungi of the soil by encouraging many younger workers, including the writer of these lines, by helping them with the identification of the fungi that they have isolated from the soil, and by devoting his whole life to the advancement of the knowledge of fungi, notably those that inhabit soils, composts, and food products, this paper is gratefully dedicated.

INTRODUCTION

It is just 30 years since the writer of these lines first dug four trenches in as many soil types on the College Farm grounds of the New Jersey Agricultural Experiment Station, in order to obtain, under aseptic conditions, samples of soil from a number of different depths. These soils were used for the study of the microbiological population; namely, the bacteria, actinomycetes, and fungi, as determined by the agar plate method using media then commonly employed in soil bacteriological laboratories. Comparatively little was known at that time concerning the nature of soil-inhabiting fungi, their numbers and distribution, and their role in soil processes. The question was even raised (1*) whether fungi are capable of growing and produce a mycelium in a normal soil: whether the fungus colonies obtained by the use of the plate method were not due, after all, to spores settling from the dust upon the soil rather than to vegetative growth present naturally in the soil. It was suggested that the mere presence of such organisms was no proof at all that they are active in the soil under normal conditions. In order to answer this and many other questions pertaining to the fungus flora of the soil and its importance in soil processes and in plant growth, new methods had to be developed and more information gained.

¹ Journal Series Paper, New Jersey Agricultural Experiment Station, Rutgers University, department of soil microbiology.

The results presented in this paper summarize the investigations carried out in the department of soil microbiology of the New Jersey Agricultural Experiment Station, Rutgers University, during the last 30 years, on the subject of fungi and their relation to soil processes. The actinomycetes, being considered as forms more closely related to the bacteria, are omitted from this review. Unasterisked numbers in parentheses refer to the Bibliography, which comprises reports from this department. References to the work of other investigators on soil fungi have been kept to a minimum. Only a very few of those that have a direct bearing on the subject under consideration are cited, in order to complete the picture presented here. In several of these publications, other references are reviewed in great detail. Asterisked numbers in parentheses refer to the appended References, publications from outside this department.

BACKGROUND

The knowledge of fungi dates back to the fundamental studies by a group of brilliant botanists including DeBary, Brefeld, and Ferdinand Cohn and followed by a number of mycologists and plant pathologists. The physiology of the fungi and their biochemical activities were investigated in detail, first by Raulin, then by Wehmer, and later by many chemists, physiologists, and microbiologists. Gradually a clear understanding of the composition of the fungi, their nutrient requirements, and their biochemical activities was obtained, and the groundwork was laid for an elucidation of their role in soil processes. Although the student of plant diseases came in contact with the soil-inhabiting fungi at an early date, he was more interested in these fungi as causative agents of disease than as participants in the many important soil processes.

It had been known from the work of Adametz, in 1886, that the fungi are represented in the soil by many species and genera, but only casual consideration was given them during the early days of microbiology. Müller had noted, in 1883, that humus-rich soils contain an abundance of fungal hyphae, and that fungus types in forest soils differ from those in peat. On the basis of these and other investigations, Ramann, in 1900, laid emphasis on the fact that acid forest soils contain an abundant fungus flora. Oudemans and Koning, in 1902, enlarged upon this concept and demonstrated by actual isolations that highly organic soils are rich both in numbers and in types of fungi.

Four extensive surveys of soil fungi were made by Hagem in Norway, Dale in Great Britain, Jensen in this country, and Lendner in Switzerland, between 1907 and 1914, the first and last being limited largely to the Mucorales. Goddard (10*) studied in 1913 the distribution of fungi in certain American soils. Although few species were isolated, he concluded that fungi occur uniformly in the soil to a depth of 14 inches and that no one form shows any specific relationship to depth of soil. These considerations led him to the further conclusion that the soil contains a constant and characteristic fungus flora.

Information on the activities of the fungi was also accumulated in 1914. Many fungi were known to be capable of decomposing cellulose, as shown by Van Iterson in 1904, by Appel in 1907, and later by Traaen, Daszewska, and McBeth and by Scales. Some of these studies pointed to the importance of fungi as humus builders in the soil. Müntz and Coudon and Marchal established, in 1893, that fungi are capable of breaking down proteins, liberating ammonia, a phenomenon later confirmed by various investigators, and elaborated by McLean and Wilson (1), at this Institution. The problem of nitrogen-fixation by fungi also aroused considerable interest, as shown by the work of Heinze, Kossowicz, and others; however, Goddard demonstrated beyond any reasonable doubt that fungi are unable to fix atmospheric nitrogen.

This information, however, was rather fragmentary. The concept of soil fungi, as a whole, appeared to be in a rather confused state, patchy and uncoordinated; the gaps were sufficiently numerous to obscure the whole picture. Proper methods were lacking for the enumeration of fungi in the soil, for demon-

strating their presence in the form of vegetative mycelium, and for determining their role in various soil processes.

When the first soil samples obtained from the trenches on the College Farm were brought to the laboratory and treated by the common plating procedure, some surprising results were obtained (2). The samples taken just below the surface soil layer gave large numbers of fungi that tended to disappear rapidly with an increase in depth. This reduction was greater than for the bacteria and actinomycetes, as brought out in table 1. The microbiological population of the

TABLE 1
*Numbers of bacteria, fungi, and actinomycetes in soil**
Thousands per gram

SOIL	DEPTH	BACTERIA	FUNGI	ACTINOMYCETES
	<i>inches</i>			
Garden	1	4,700	400	700
	4	4,500	700	800
	8	3,500	600	1,200
	12	720	50	440
	20	210	30	290
	30	160	40	510
Orchard	1	4,600	400	600
	4	4,500	500	1,300
	8	1,560	90	480
	12	670	30	470
	20	130	20	540
	30	90		460
Timothy	1	15,400	1,110	1,300
	4	7,000	700	1,100
	8	1,710	130	430
	12	1,040	40	270
	20	690	50	340
	30	160	20	200

* This table formed part of a paper presented at the 17th Annual Meeting of the Society of American Bacteriologists, held at Urbana, Ill., on Dec. 28-30, 1915; only an abstract of the paper was published (2).

soil, especially that of the fungi, was found to be limited chiefly to the upper 8 to 12 inches of soil. The dilutions of soil used for the preparation of the plate were rather high 1:10,000 to 1:1,000,000—in order to provide enough colonies of bacteria and actinomycetes to make the count statistically accurate. Since the numbers of fungi were much smaller than those of the other groups, the fungus count was not only unrepresentative but far from accurate. When low dilutions of soil were used (1:100), there were so many colonies of bacteria and actinomycetes on the plates, that the growth of the fungi was virtually eliminated. Thus, the preliminary study of the abundance of the fungus population in the soil revealed the need for better methods of studying these organisms.

The subsequent investigations dealt with the distribution of fungi in different soils and with the influence of ecological factors; namely, climatic, soil or edaphic, and biotic or living, upon their nature and abundance (6). An attempt was also made to gain an insight into the biochemical activities of the fungi. Gradually, a better understanding of these organisms, their relation to other soil microorganisms, and their role in soil processes was gained.

PROBLEMS CONSIDERED

As this information began to accumulate, a number of problems arose. They are listed here not necessarily in the sequence in which they were considered or investigated, but in the order in which one would have liked to study them, after benefiting from three decades of experience with these organisms.

To establish whether fungi live in the soil and produce there a vegetative mycelium.

To develop a method for the enumeration of soil fungi, or at least those forms that are capable of producing growth on artificial culture media.

To gain detailed information concerning the nature of the fungus population of the soil, and to establish whether it is characteristic of the soil as a whole or whether each soil possesses its own distinct population, depending on the nature of the soil, the climate, and surface vegetation.

To coordinate the biochemical activities of the fungi with their role in the processes of decomposition of plant and animal residues, transformations and syntheses that have a bearing upon soil reactions, notably the liberation of the essential nutrient elements in available forms, and in the formation of soil humus.

To determine the relationship of the fungus flora to the other members of the soil microbiological population.

To study the relationships of soil fungi to the growth of higher plants.

The results obtained from the study of these and many other problems bearing upon the activities of the soil fungi were reported in various scientific journals and special publications. They are summarized here in order to present a concise and logical picture of the accumulated knowledge of the fungus population of the soil and its role in soil processes and in plant growth. For a full interpretation of the results, the reader is referred to the original publications, where ample credit is given to other workers in the field.

Do fungi produce vegetative mycelium in the soil?

When insufficient precautions are taken in obtaining soil samples under aseptic conditions and in preparing the plates, many of the fungi appearing on the plate may be of dust origin. In addition, the common plate method for the enumeration of the soil fungi appeared to be subject to many limitations, especially the great variability in the numbers of fungus colonies, as compared with those of bacteria and actinomycetes. Because of this, the very nature of the fungus flora of the soil as a native population characteristic of this natural substrate was questioned. The fact, however, that the distribution of these fungi is not limited to the surface layer of the soil but occurs throughout a considerable depth, and the fact that many species were found to have a very wide distribution, having been reported from many parts of the world, tended to emphasize that

these organisms are normal soil inhabitants rather than mere accidental invaders which may have been brought into the soil with the dust of the air or with the plant and animal wastes.

An attempt was first made, therefore, to determine whether fungi are present in the soil in a vegetative or a mycelial state. Samples of soil were taken under aseptic conditions. Minute clumps were placed on the surface of suitable agar media in Petri dishes. The growth of the mycelium from the soil particles into the agar was carefully examined. Certain fungi were found to grow out very rapidly from the soil and produce an extensive mycelium in the agar medium, within a period of incubation of 24 hours or less, at 28-30° C. The tips of the hyphae of this mycelium were transferred upon sterile agar slants, and the organisms cultured and identified. The assumption was thereby made that the fungus mycelium present in the soil grows out into the agar more rapidly than do the spores of such fungi. This was checked by inoculating agar plates with mycelium of certain fungi obtained in pure culture, and the rate of its growth compared with that of the spores of the same fungi. This method made possible the isolation from the soil of species of *Mucor*, *Zygorhynchus*, *Rhizopus*, and *Trichoderma*; these organisms were believed to be present in the soil in the form of viable vegetative mycelium, since they had been isolated from a variety of soils taken great distances apart, as well as from different depths of the same soil (3).

In the course of years, four other methods of approach to this problem were developed:

1. By treating a soil with volatile antiseptics or with heat, the fungi were more readily eliminated than the bacteria and actinomycetes; this was accompanied by a considerable reduction in the rate of decomposition of cellulose added to such soil. As a result of such treatment large quantities of fungus mycelium in the soil were killed and could be attacked by the soil bacteria, resulting in the liberation of large amounts of nitrogen as ammonia (22).

2. By acidifying the soil, either through the use of acid-reacting chemicals, such as ammonium sulfate, or by the introduction of sulfur, which on oxidation gives sulfuric acid, the growth of bacteria and actinomycetes was discouraged without damaging and, in some cases, even favoring the growth of the fungi (16, 17).

3. By the use of special acid agar (14), it was found that soils collected from all over the North American continent always yielded certain specific organisms. Many of these organisms do not usually occur in any other natural substrate, thus further pointing to their being characteristic of the soil.

4. The addition to the soil of fresh organic materials rich in cellulose brought about considerable stimulation of the development of soil fungi (24).

Fungi were also found capable of bringing about in sterile soil many processes of decomposition and synthesis that are characteristic of natural soils. These facts left no doubt, therefore, that fungi must be considered as typical soil organisms, taking an active part in many of the normal soil processes.

By the use of a special staining technique, Conn (2*) later demonstrated that nearly all soils contain an abundance of fungus mycelium, in the form of filaments or fragments. McLennan (16*) found that when a soil was dried in a

desiccator over calcium chloride, a marked reduction in the number of fungi occurred. The reduction was ascribed to the destruction of the fungus mycelium, and the conclusion was reached that the fungus population of the soil is largely in a vegetative state.

The specific nature of the fungus population is modified by soil type, as well as by climatic and vegetation factors. Forest soils rich in bases (deciduous forests) were shown to contain an abundant population of Mucorales, largely of the *M. flavus* type; somewhat more acid soils (mixed forests) contain the *M. ramannianus* group; and the very acid (raw-humus forest) soils are characterized by a fungus flora of the *Zygorhynchus muelleri* type (12*).

Kubiena (15*) finally demonstrated, by direct microscopic examination, that a large number of fungi are capable of producing an extensive vegetative mycelium and even of sporulating in the soil. Certain species of fungi were found to be particularly abundant. He was thus able to confirm the early observations made in this laboratory (3) that the soil contains an autochthonous fungus flora. The qualitative and quantitative composition of this flora is modified by the nature of the soil, its cultivation, and the crop grown (76).

These facts together with others that will be discussed later can lead to but one conclusion, namely, that many fungi are to be considered as typical soil organisms, that they lead a normal vegetative life in the soil, and that they play a highly important part in many of the soil processes.

Enumeration of fungi in the soil

It has already been pointed out that the determination of the abundance of fungi in the soil by the common agar or gelatin plate method used for the enumeration of bacteria is open to considerable criticism. In order to permit the development of a maximum number of bacteria, very high dilutions of soil are commonly employed. Although the fungi grow readily on the agar media that are used for the development of the bacteria, much lower dilutions of soil must be used for the fungi in order to satisfy the same statistical requirements for the two types of colonies, namely, a sufficiently large number of colonies, 30 to 100, per plate to reduce the factor of great variability.

This was accomplished (14) by the acidification of a suitable agar medium to pH 3.8 to 4.0. The acid reaction prevents the development of most of the bacteria and actinomycetes without affecting appreciably the growth of the fungi. If the reaction is adjusted first, care must be taken to sterilize the medium at not more than 8 pounds' pressure, for 30 to 45 minutes. The reaction can also be adjusted after sterilization, by the use of sterile acid. A satisfactory medium, which has since become known as "fungus agar," was thus developed. This medium consisted of 25 gm. agar, 10 gm. glucose, 5 gm. peptone, 1 gm. KH_2PO_4 , 0.5 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 1,000 ml. distilled water, pH 4.0. In order to eliminate the use of peptone, which tends to favor the growth of spreaders, a modification of this medium was suggested (11*), consisting of 20 gm. glucose, 2 gm. asparagine, 1 gm. KH_2PO_4 , 0.5 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 gm. NaCl, 0.1 gm. FeCl_3 , 25 gm. agar, 1,000 ml. water, pH 3.8 to 4.0.

This method has been utilized extensively for the study of the abundance of fungi in variously treated soils. Not only have definite differences in numbers been found, as brought out in table 2, but enumerations of fungi made on the same soils during a number of years, even by different investigators visiting the laboratory, yielded highly consistent results. It is felt that greater dependence can be placed upon the enumeration of fungi in the soil by the use of the acid agar method than even upon the enumeration of bacteria, because, in comparison with fungi, many more kinds and greater numbers of bacteria fail to develop on the common agar media.

On the other hand, the plate method for the enumeration of fungi suffers from several important limitations: first, certain large groups of fungi like the Basidiomycetes fail to develop on the plate or develop to only a limited extent, whereas

TABLE 2
Influence of soil treatment upon the abundance of fungi

TREATMENT OF PLOT	pH OF SOIL	CARBON IN SOIL	NUMBER OF FUNGI PER GRAM	
			July 18	September 22
		<i>per cent</i>		
Minerals only (4A).....	5.6	1.26	31,000	45,600
Stable manure + minerals (5A).....	5.4	1.44	54,000	91,000
No fertilizer or manure (7A).....	4.5	0.93	56,000	63,000
Nitrate + minerals (9A).....	5.5	1.13	47,000	45,900
Ammonium sulfate + minerals (11A).....	4.1	1.21	115,000	107,900
Stable manure + nitrate + minerals (18A).....	5.5	1.36	73,000	87,600
Minerals only (19A).....	5.2	1.01	61,000	48,200
Lime only (7B).....	6.4	1.02	28,000	16,900
Ammonium sulfate + minerals + lime (11B).....	5.8	1.06	44,000	34,200
Minerals + lime (19B).....	6.7	0.95	32,000	26,200

the Phycomycetes give only a limited number of colonies on the plate as compared with the abundance of their vegetative growth; second, the method does not differentiate between the numbers of colonies produced from spores and those produced from pieces of vegetative mycelium. Nevertheless, despite these limitations, the plate method enables a more or less accurate determination of the nature of the fungus population of the soil, even if only in its approximate state.

The reaction of the soil and its organic matter content were found to be the two most important factors controlling the abundance of fungi. In the plots of table 2, the greater the acidity of the soil, the greater, in most cases, was the number of fungi; the most acid soil, having a pH of 4.1, contained 111,450 fungi per gram, and the least acid, pH 6.7, contained 29,100 fungi. The higher the organic matter content of the soil, the reaction being the same, the greater was

the number of fungi; the manured soils are characterized, therefore, by a more abundant fungus population than the soils receiving mineral fertilizers only.

In addition to the foregoing factors, two others may be added; namely, moisture and temperature. Both influence the abundance and the nature of the fungi predominating in a certain soil. This was brought out in a study of the influence of moisture upon the production of ammonia by pure cultures of fungi (4), wherein 50 to 65 per cent of the moisture-holding capacity of the soil was found to be optimum for the growth of these organisms, and above and below that optimum there was a gradual drop in the production of ammonia. The effect of temperature can be illustrated by composting experiments (53). Some of these fungi are thermophilic, being capable of growing at 50°C.; however, most of them are mesophilic and are rapidly depressed by higher temperatures, especially above 50°C.

Studies of the decomposition of various plant materials by pure cultures of fungi, as compared with that of the total soil population, were begun by Neller in this laboratory in 1918 (9) and were later extended (54). Either CO₂ evolution or the rate of destruction of the individual chemical plant constituents was used as a measure of decomposition. These studies led to the conclusion that fungi must be considered as among the most active members of the soil population in the decomposition of plant residues.

One may thus conclude that the fungi are abundantly represented in the soil by an extensive vegetative mycelium, as well as by a number of spores, possessing potential development of these organisms. The actual abundance of these organisms is controlled by a number of factors, including soil reaction, aeration, moisture, and temperature, as well as by the available food supply, comprising the nature and abundance of the organic matter.

Nature of the fungus population of the soil

Many of the fungi isolated from the soil were found to be typical soil inhabitants and to occur but seldom in other substrates. Other fungi, however, are only temporary invaders, even if they are able to survive in the soil for a very long time. The chief problem, therefore, still remained, namely, to obtain a clear picture of the nature of the fungus flora of the soil, and to determine to what extent it is influenced, both quantitatively and qualitatively, by the composition of the soil as well as by the nutritional, environmental, and ecological soil factors.

In an extensive survey on the fungus population of the soil (6, 7), 31 genera were isolated and identified, and some of these were represented in the soil by many species. On comparing the fungi previously isolated by Koning in Holland, by Dale in Great Britain, and by Jensen, Goddard, McLean, and Wilson in the United States with the representative groups of fungi isolated in these studies, the conclusion was reached that four genera, *Aspergillus*, *Penicillium*, *Mucor*, and *Trichoderma*, are most abundant. These have been isolated from various soils in different parts of the world. Eight other genera (*Acrostalagmus*, *Alternaria*, *Cephalosporium*, *Cladosporium*, *Fusarium*, *Rhizopus*, *Verticillium*,

Zygorhynchus) were somewhat less abundant but were also of very common occurrence. In all, more than 200 species of fungi, representing 42 or more genera, have now been isolated from the soil and described.

A forest soil was found to contain but few Mucorales, but a large number of Trichodermae and Penicillia; an orchard soil gave many Mucorales, no Trichodermae, and but few Penicillia; a well-cultivated garden soil contained many fungi, without any one single group predominating. The Mucorales were found to be more abundant in colder climates and the Aspergilli in warmer regions; the Trichodermae were extensively distributed in acid and in waterlogged soils. These results were later confirmed (11*), when forest, moor, and heath soils in Denmark were shown to contain a characteristic flora of Trichodermae, whereas the flora of field, marsh, and uncultivated mineral soils consisted largely of Mucoraceae.

The more fertile soils contained a greater number as well as a greater variety of fungi than the less fertile soils. A study of permanent mangold and wheat fields at Rothamsted also gave a direct correlation between soil fertility and the abundance of fungi and actinomycetes (24*). When fresh plant materials were added to the soil, the numbers of fungi were greatly stimulated; very often a sequence of forms was reported, depending on the chemical composition of the plant materials added and the extent of their decomposition (23*).

As a result of studies of the fungus flora of soils throughout the world, many new genera of fungi represented by numerous species were added to the previous lists. Cholodny (3*) demonstrated, by the use of the contact slide method, that forest soils contain an abundance of fungi present both as vegetative mycelium and in the form of spores. Some of the fungi, notably species of *Trichoderma*, are so characteristic of the soil that their presence has often been taken to be an index of the fungus population as a whole and of its distribution (20*). The synthetic acid agar originally developed for the enumeration of fungi in the soil (15) has been recommended (9*) for the isolation of fungi from the soil; not only are the bacterial colonies thus eliminated, but the growth of the fungi is favored. Gilman and Abbott (9*) in 1927 and Niethammer (18*) in 1937 coordinated and summarized the existing information on the fungus population of the soil. Some 61 or more genera were listed. Some of these genera received particular attention, either because of their wide distribution in nature or because of their great economic importance. These include the genera *Penicillium* (27*), *Aspergillus*, *Mucor*, *Rhizopus*, the yeasts (25*), the mushroom fungi (8*), the mycorrhiza fungi (17*, 21*, 5*), and the plant-disease-producing fungi (7*, 22*).

These and other investigations definitely established the fact that fungi form a very large and heterogeneous group of soil microorganisms permeating the whole surface layer of the soil with their mycelium, their numbers and types gradually decreasing in the lower soil layers. Some of the fungi are widely distributed in nature, and others are limited to certain habitats. The specific nature of these organisms is influenced by the abundance and nature of the soil organic matter, as well as by soil and climatic conditions, by surface vegetation, and by soil management.

Biochemical activities of fungi and their bearing upon soil processes

Among the many chemical processes brought about by fungi, which have been considered to have an important bearing on soil processes, the following have received the greatest attention: (a) the fixation of atmospheric nitrogen, (b) the decomposition of proteins and protein-rich materials, accompanied by the liberation of ammonia, and (c) the decomposition of cellulose; in addition to these, fungi also play a highly important role in many other transformations; namely, (d) the decomposition of plant and animal residues in soils and in composts, (e) the decomposition of the soil organic matter or soil humus, accompanied by the liberation of CO_2 , (f) the contribution of the fungus mycelium to the synthesis of the soil humus.

Although Goddard (10*) apparently established the fact that soil fungi are totally incapable of fixing atmospheric nitrogen, it was felt that these results could be profitably checked. An attempt to do this was made in the first study of the distribution and activities of soil fungi (6). Five species, representing as many distinct genera, were used for this purpose. The results obtained fully confirmed those of Goddard, and the conclusion was reached that soil fungi should not be considered as taking any part in the nitrogen-fixing complex of the soil. Even where positive increases in fixed nitrogen were obtained, the amounts were so small as to be considered to fall within the limits of analytical errors. Fungi were found to be capable, however, of producing large amounts of ammonia from protein-rich materials. Most of the organisms tested were capable of liberating more nitrogen as ammonia than even the strongest ammonifying bacteria, under similar conditions. *Trichoderma köningi* was, in this respect, the most active organism; the *Penicillia* differed with the species, most of them being comparatively weak ammonifiers; the *Mucorales* were fairly active, different species not differing greatly from one another.

Available carbohydrates were found to have an important influence upon protein decomposition by microorganisms, including fungi (8). This influence affects both the rate of ammonia formation in the decomposition of complex plant and animal residues and the synthesis of fungus mycelium, which contributes to the formation of soil humus. These processes are also markedly influenced by the carbon-nitrogen ratio of the nitrogenous materials (26). A comparison of the capacity of a soil fungus and of a soil bacterium to decompose plant proteins, as influenced by the presence of glucose, is brought out in table 3. The fungus showed a much narrower ratio of protein decomposed to cell substance synthesized than did the bacterium (64).

Although it was known since the work of Van Iterson, in 1904, and of Appel, in 1907, that many soil fungi are capable of decomposing cellulose, the information was not sufficiently coordinated, either because of the limited amounts of cellulose destroyed by the organisms tested or because of the insufficient differentiation between the true cellulose and the hemicelluloses in the plant materials. In the first survey made of the fungus population of the soil (6), it was found that most of the isolated fungi were very strong cellulose-decomposers, 15 out of 22 organisms tested being capable of bringing about this process rather

rapidly. The cellulose-decomposing fungi were far more active in this respect than the cellulose-decomposing actinomycetes and bacteria, at least under the particular experimental conditions. A marked correlation was obtained (21, 28, 30) between the amount of cellulose decomposed and the growth of the fungus, the latter being measured by the quantity of nitrogen transformed from an inorganic into an organic form by the mycelium (table 4). The ratio of cellulose

TABLE 3
Decomposition of plant proteins by a fungus and a bacterium

PROTEIN	ORGANISM	GLUCOSE ADDED	PROTEIN DECOMPOSED	GROWTH OF ORGANISM
			mgm.	mgm.
Edestin.....	<i>Trichoderma</i>	—	541	167
Edestin.....	<i>Trichoderma</i>	+	375	359
Edestin.....	<i>B. cereus</i>	—	622	52
Edestin.....	<i>B. cereus</i>	+	506	
Gliadin.....	<i>Trichoderma</i>	—	854	151
Gliadin.....	<i>Trichoderma</i>	+	495	460
Gliadin.....	<i>B. cereus</i>	—	905	
Gliadin.....	<i>B. cereus</i>	+	606	203
Zein.....	<i>Trichoderma</i>	—	339	91
Zein.....	<i>Trichoderma</i>	+	633	355
Zein.....	<i>B. cereus</i>	—	853	15
Zein.....	<i>B. cereus</i>	+	276	153

TABLE 4
Decomposition of cellulose by Trichoderma sp.

INCUBATION	CELLULOSE DECOMPOSED	CO ₂ LIBERATED	GROWTH OF FUNGUS	NITROGEN ASSIMILATED	RATIO OF CELLULOSE DECOMPOSED TO NITROGEN ASSIMILATED
days	mgm. C	mgm. C	mgm.	mgm.	
7	207	78	291	18.9	24:1
14	409	126	640	27.4	33:1

decomposed to nitrogen consumed by the fungi was about 30:1. This ratio was later found to have a bearing upon the extent of liberation of nitrogen in the form of ammonia in the decomposition of plant materials (40), especially in green manures (42), in composts of plant residues (44), or in stable manures (45).

The addition of cellulose to the soil had a marked effect upon the development of fungi, as compared with the bacteria and actinomycetes. This was especially true where an available source of nitrogen was also added. The controlling

effect of the nitrogen upon the decomposition of the cellulose and upon the development of the fungi was very striking; this led to the conclusion that the liberation of nitrogen in a given soil is affected, if not completely controlled, by the rate at which the added cellulose can be decomposed. This process was measured either by the rate of evolution of CO_2 from the cellulose or by the extent of disappearance of the cellulose. The treatment of the soil with disinfectants (19) brought about a sharp reduction in the number of fungi, which was accompanied by a reduction in the amount of cellulose decomposed thus emphasizing further the role played by the fungi in the destruction of cellulose in the soil (21, 28, 30).

The stimulating effect of cellulose upon the fungus population is greatly influenced by the soil reaction (21, 31). This confirms the earlier observations of the effect of reaction upon the nature of the fungus flora of the soil. Whereas the addition of cellulose to a California soil of pH 7.5 resulted in hardly any in-

TABLE 5
Decomposition of washed horse manure by pure cultures of fungi

PLANT CONSTITUENT	TOTAL IN CONTROL	MATERIAL DECOMPOSED* IN 51 DAYS BY		
		<i>Trichoderma</i>	<i>Coprinus</i>	<i>Agaricus</i>
	mgm.	mgm.	mgm.	mgm.
Total material.....	11,779	555	2,378	1,015
Water-soluble organic matter.....	312	+96	+268	+372
Hemicelluloses.....	1,326	8	444	+396
Cellulose.....	3,334	235	2,224	479
Lignin.....	3,183	54	518	555

* + indicates increase.

crease in the numbers of fungi, a New Jersey soil having a pH of 5.2 showed a very marked increase. The conclusion was reached, therefore, that in acid soils, fungi are the primary agents concerned in the decomposition of cellulose (41).

In a study of decomposition of complex plant materials, such as horse manure, by pure cultures of fungi (54), various organisms were found to differ greatly in their ability to attack the specific chemical constituents (table 5). *Coprinus* brought about greater decomposition of cellulose than either *Agaricus* or *Trichoderma*. The total decomposition of the individual chemical constituents of the manure was found to exceed the amount of total material decomposed. This was due to the extensive synthesis of mycelium by these fungi, as illustrated by the increase in the water-soluble constituents in the residual material. Both the *Agaricus* and the *Coprinus* also decomposed considerable amounts of lignin. Although these three fungi are strong cellulose-decomposing forms, each possesses its own characteristic mechanism or capacity to attack the various chemical constituents of the plant material.

In a further study of the decomposition of complex plant materials by micro-

organisms, a larger number of organisms, was used and their action was compared with that of a complex soil population, as found in a soil suspension. This study brought out the fact that some fungi, as represented by the *Mucorales*, do not decompose either cellulose or lignin. Other fungi, like *Humicola*, were found to decompose cellulose but not lignin when no available nitrogen had been added; the addition of nitrogen greatly stimulated decomposition of plant materials by both the pure and the mixed cultures. None of the pure cultures brought about as much decomposition of the cellulose as did the complex soil population.

In the process of decomposition of plant materials, considerable fungus mycelium is synthesized. Cellulose and lignin supply the energy to the fungi, and thus play an important part in the preservation of the nitrogen in soils and in composts (74). The freshly synthesized cell material is not resistant to further decomposition but undergoes in the soil rapid attack by various bacteria and other organisms. The resulting products comprise mineralized elements and compounds that can be used by higher plants, slimy substances that have a binding effect upon the mineral constituents of the soil (13*), and certain compounds that enter into the humus complex of the soil. The binding effect of the fungi and their products upon the finer soil particles helps to prevent soil erosion (102, 107, 109, 113, 116).

The role of fungi in the decomposition of plant and animal residues in soils and in composts thus involves a large number of reactions, some of which are still but vaguely understood. Many transformations, however, have been clearly elucidated, including the decomposition of humus (25), of soil organic matter as a whole (55, 56), of cellulose (21, 28, 30, 31, 34, 35, 41, 86, 105), of hemicelluloses (55, 56) including polyuronides (68), of lignins (78, 90), and of proteins (26, 64); the liberation and assimilation of nitrogen, accompanied by cell synthesis; and the liberation of phosphorus (100). Most of these fungi are mesophilic, but a few are thermophilic (95, 97). Many of the processes carried out by fungi cannot be separated from corresponding reactions of other groups of soil microorganisms, especially actinomycetes and bacteria.

Associative and antagonistic effects of soil fungi

The ability of soil fungi to inhibit the growth of other fungi and bacteria, and even bring about their destruction, has long been recognized (19*, 81, 106). Until very recently, most attention was focused on the significance of this process in the control of plant diseases that either originate in the soil or are brought into it. Recently, attention has been largely directed to the production of antibiotic substances by fungi (130). Through their ability to produce such agents, fungi are beginning to play an important role in controlling a variety of bacterial infections in man and in animals. Illustrations include the production of penicillin by fungi belonging to the *P. notatum*, *P. chrysogenum* (6*), and other groups (122); of gliotoxin by members of the *Trichoderma*, *Gliocladium* (26*), and *A. fumigatus* groups (124); and of clavacin by a large number of fungi (125).

The principle of the acid fungus agar used for the isolation of fungi from soil and composts has been adapted to the isolation of organisms antagonistic to

bacteria (115). Washed agar, to which phosphate, glucose, and a suspension of living bacterial cells were added, is acidified to pH 4 and used for plating purposes. The nature of the fungi that develop on such plates depends entirely on the nature of the bacterium added to the medium. Gram-positive bacteria, notably *Sarcina lutea*, *Bacillus subtilis*, and *Staphylococcus aureus*, give rise, on the plates, to very clear zones surrounding the colonies of the antagonistic fungi. On the other hand, gram-negative bacteria result in rather limited zones, although some bacteria like *Pseudomonas fluorescens* are also suitable for this purpose.

By the use of this method, it was possible to isolate more than 160 strains of fungi, representing many genera and species, capable of inhibiting the growth of bacteria and of producing a variety of antibiotic substances. These fungi were divided into nine groups, as follows:

TABLE 6
Bacteriostatic action of several antibiotic substances upon different bacteria
Activity in dilution units per gram of material

SUBSTANCE	TEST ORGANISM					
	<i>S. aureus</i>	<i>M. phlei</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>Ps. aeruginosa</i> I	<i>Ps. aeruginosa</i> II
Penicillin.....	5,000,000	7,500	19,000,000	<5,000	0	0
Chaetomin.....	400,000	800,000	400,000	0	0	0
Clavacin.....	50,300	67,000	65,000	100,000	5,000	7,500
Fumigacin.....	303,000	91,000	200,000	0	0	0
Actinomycin.....	6,000,000	4,000,000	60,000,000	15,000	0	0
Streptothricin.....	500,000	300,000	1,000,000	100,000	1,000	5,000
Streptomycin*....	100,000	600,000	100,000	30,000	3,000	6,000

* This was a much cruder preparation than streptothricin; in order to compare the two, it is necessary to multiply all the results for streptomycin by 3.33, with *E. coli* as unity.

1. *Chaetomium* group. A single representative, later identified as *C. cochliodes*, was isolated during this survey. The organism produces an antibiotic substance that is largely active against gram-positive bacteria and that has been designated as *chaetomin* (132, 133).²

2. *Aspergillus fumigatus*. Some fifteen strains of fungi belonging to this group were isolated from the soil. These organisms produce as many as four antibiotic substances; namely, spinulosin, fumigatin, *fumigacin* (120, 124), and gliotoxin (124), which differ greatly in the extent of their activity and in the nature of the antibacterial spectrum. The first three are largely active against gram-positive bacteria, whereas the last acts also upon gram-negative organisms.

3. *Aspergillus clavatus*. Three strains of this organism, isolated from composts, were found to produce a powerful antibiotic substance active against both gram-positive and gram-negative bacteria. This substance has been described as *clavacin* (119, 120), and was found to be identical with claviformin, patulin, and clavatin, described by other investigators (125). It is produced by a large number of other fungi.

4. *Aspergillus flavus-oryzae* group. Members of this group of fungi are capable of producing two antibiotic substances, aspergillic acid and a penicillin-like substance, variously

² Italics indicate that the substance was first studied in our laboratory and described by us.

described as flavatin, flavicin, and flavacidin. The latter is produced in complex organic media, especially when grown in a submerged and agitated state (122).

5. *Penicillium luteum-purpurogenum* group. A large number of organisms belonging to this group have been isolated and found to have antagonistic properties. Some produce substances of the penicillin type and others of the clavacin type.

6. *Penicillium notatum*-*P. chrysogenum* group. Members of this group of fungi produce two antibiotic substances, one of which is the now classical penicillin and the other a glucose-oxidase, which has been variously described as penatin, *E. coli factor* (115), notatin, and penicillin B. In the early studies (6), several strains of this group of fungi were isolated from a number of different soils. These organisms must be considered as typical soil inhabitants (131).

7. *Trichoderma*. A substance designated as gliotoxin is produced (27*) by some strains of this group of fungi.

8. *Fusarium-Cephalosporium* group. Many strains of these two genera of fungi have been isolated from the soil and found capable of producing antagonistic effects against bacteria. None of these organisms has been studied in further detail, however, and no antibiotic substance has been isolated.

9. Miscellaneous group of fungi, comprising a variety of unidentified species capable of antagonizing the growth of various bacteria.

The nature of the fungus strain and the conditions of culture have a marked effect not only on the amount of antibiotic substance produced, but often on its very nature. This was found to hold true, for example, for penicillin-producing strains of *P. notatum* (131) and *A. flavus* (122), clavacin-producing *A. clavatus* (119), and others. The antibiotic substances not only possess bacteriostatic properties but exert also a marked bactericidal action (134), different bacteria varying greatly in the degree of their sensitivity to each substance.

Although most of the antibiotic substances that have been studied so far are largely active against bacteria (table 6), some have also been found to exert a marked effect upon fungi, including such important parasites as *Ceratostomella ulmi* (123). It may be of interest to note that various fungi also possess the capacity of killing protozoa and nematodes (4*).

A large number of soil fungi thus are found capable of controlling the development of various other microorganisms. This may prove to be of particular importance in keeping the soil in a sanitary state, at least so far as many of the bacteria capable of causing human and animal infections, and possibly bacteria causing plant diseases (127), are concerned. To what extent this antagonistic action of fungi may prove to be injurious to some of the useful soil organisms, such as the root nodule bacteria of leguminous plants, still remains to be determined.

The full significance of these findings in terms of soil processes must await the more careful coordination of the results. Although the problems of infection and disease have made it necessary to emphasize those aspects that have a direct bearing upon the isolation of antibiotic substances (135), there is no doubt that much of the information obtained in these studies may prove to have a bearing upon the nature and abundance of the soil population in its influence upon useful organisms as well as upon those fungi and bacteria that cause animal and plant diseases. Cooperative studies on the control of the larvae of the Japanese beetle in the soil by means of the fungus *Metarhizium* and especially of certain bacteria

causing the so-called white milky disease of the beetle larvae have yielded very encouraging results (108).

Fungus population of the soil in relation to growth of higher plants

The relations of the fungus population of the soil to the growth of higher plants represent four distinct aspects: first, the occurrence of fungi in the rhizosphere of the plants; second, the formation by some fungi of associations with the root systems of various plants, known as mycorrhizae (17*, 21*); third, the causation of plant diseases by different soil-inhabiting fungi (7*, 22*); and fourth, the influence of saprophytic soil fungi upon fungi producing plant diseases. Only the first of these problems has received detailed consideration. The other three phenomena, therefore, are only briefly mentioned here, despite their great economic importance.

In a study begun by Starkey in this laboratory in 1928, it was found (48, 49) that the filamentous fungi appeared to be less affected than either the bacteria or the actinomycetes by root development of higher plants. As determined by the plate method, there was only a moderate increase in the abundance of fungi in the vicinity of root development. An investigation of the relative abundance of fungi in soils at various distances from the root surfaces (61, 62) indicated that the numbers of fungi were not appreciably greater in soils around the plant roots than in soil obtained at some distance away. The actual superficial root tissues, however, showed evidence of considerable fungus development, yielding, in some cases, ten times as many colonies of fungi as soil obtained from the rhizosphere. Further evidence of the effects of roots on fungus development was obtained by the use of buried slides (92), according to the procedure of Cholodny (3*). There was abundant fungus development about root hairs and small roots, but fungus growth was not so profuse as that of bacteria. The fungi appeared not only on the residues of the dead roots and root hairs, but also on roots that apparently were developing actively. The filaments grew near the surface of the roots and also penetrated intracellularly and intercellularly. In regions where root tissue was disintegrating there was a profusion of bacteria, actinomycetes, and fungi, the last appearing as vegetative mycelium and as spores. The results indicated that higher plants, through their roots, have a much greater influence on fungus development than was evident from the initial results, obtained by the use of the plate method, which must be considered as somewhat inadequate for this purpose.

The characteristics of some of the fungus structures occurring on the buried slides were different from those of the fungi commonly encountered on agar plates inoculated with soil. It was concluded that many of the typical soil fungi are not recovered from the soil on the agar plates or that the fungi show different growth characteristics in the soil. Even in regions of the soil where there was no appreciable development of plant roots, there was a considerable amount of fungus mycelium and a variety of fungus spores. Some spores occurred in aggregates, and others were very much dispersed. Fungus growth was encountered about bits of decomposing plant material and insects.

There were evidences of extensive bacterial development about the fungus mycelium. In some instances the bacterial cells were scattered along the hyphae. Sometimes small aggregates of cells studded the mycelium. The most striking effect was the development of large dense aggregates composed of hundreds of small coccoid bacterial cells on the hyphae. Although the bacterial development was doubtless concerned in destruction of the fungus hyphae, in many instances the large aggregates of bacteria probably were developing upon the organic materials excreted by the fungi. These results suggest the following explanation for the nonpersistence of the mycelium of certain fungi in the soil: certain environmental conditions lead to rapid vegetative development of the fungi, and after the food supply is exhausted or when there is a change in the environmental conditions, the mycelium is destroyed by other soil microorganisms.

A number of theories have been proposed (7*, 38) in regard to the control, by stimulating the development of antagonistic soil microorganisms, of fungi producing plant diseases. One of the best means of accomplishing favorable results consists in adding fresh plant materials in the form of green manures, stable manures, or composts. These favor the development in the soil of a large number of fungi and bacteria, which in their turn bring about the inhibition of growth and often actual destruction of the disease-producing organisms. This was shown (14*) to hold true of the cotton root-rot fungus and many others.

Miscellaneous problems on the occurrence and activities of fungi

Among the various miscellaneous problems dealing with fungi, isolated from the soil or from other substrates, investigated during the last three decades, the following deserve consideration:

Production of organic acids by fungi. The formation of lactic (85, 91) and fumaric (93, 94) acids by several species of *Rhizopus* resulted in development of practical processes for the manufacture of these two acids. A patent was obtained (114) for the manufacture of fumaric acid, both by surface and by submerged growth.

Enzymes of fungi. Enzymes produced by fungi, including proteolytic (11), amylolytic (13), and lipolytic (77), were investigated at various times, often from the point of view of application of such enzymes to industry, and a monograph dealing with enzymes of microorganisms was published (18).

Acid-tolerant fungi. In connection with the study of damage done by fungi to certain textile products in baths containing sulfuric acid and copper sulfate, two fungi were isolated (121) that were capable of growing in 2.5 N sulfuric acid and in a saturated solution of copper sulfate. These fungi were later identified as *Acontium velatum* and a member of the *Dematiaceae*.

Nutrition of fungi. The metabolism of various fungi was investigated at different times, from the point of view of the utilization of specific nutrients by fungi, the effects of certain elements such as heavy metals (98) on the growth of fungi, the production of organic acids and other metabolic products, or the development of a proper medium for the growth of economically important fungi.

In the study of the nutrition of the edible mushroom (57, 58, 65, 66, 72), it was found that *Agaricus campestris* is capable of utilizing the lignin and lignin-like materials in the composts, as shown in table 5. Since the composting of plant residues and stable manures leads to an accumulation of lignin and to a reduction in the cellulose, it was suggested that the major purpose of composting such materials is to bring these two reactions, thus favoring the development of a compost required by the mushroom fungus. This fungus utilizes largely the lignin, the cellulose being consumed to only a limited extent.

Role of fungi in soil processes and in plant nutrition

One is justified in concluding that, because of their great abundance in the soil and their many and varied activities, fungi play a very important role in soil transformations and in the growth of higher plants. These effects may be summarized briefly as follows:

Fungi break down complex plant and animal residues, reducing them to a mineralized state and liberating the essential elements in forms available for plant growth. They also transform some of the plant and animal constituents to humus, which is resistant to rapid attack by microorganisms and becomes a part of the soil system.

Fungi readily attack proteins, both in a free state and in the form of plant and animal residues, liberating some of the nitrogen as ammonia. A part of the nitrogen is stored in the newly synthesized fungus cell material. This is especially true when, in addition to the proteins, carbohydrates are present, thus permitting the synthesis of considerable mycelium in the soil.

Many fungi are capable of bringing about the rapid destruction of cellulose and hemicelluloses, but not of the lignins, in the plant materials. In consequence, the lignins tend to accumulate in the soil in the process of decomposition of the plant residues.

Through the synthesized mycelium and the accumulation of the residual lignin, fungi contribute directly to the formation and accumulation of humus in the soil.

Soil humus is not absolutely resistant to further decomposition by microorganisms. Many fungi are capable of bringing about a gradual destruction of the humus, liberating the carbon as CO₂ and the nitrogen as ammonia. Certain fungi, like *Agaricus campestris* and *Coprinus*, have a special capacity of decomposing lignins and the resistant humus complexes.

Soil fungi form various associations with plants, ranging from direct symbiosis to definite parasitism.

Certain fungi that have the capacity of surviving in the soil, where they may lead a normal life, are capable of attacking higher plants, thus resulting in a large number of important plant diseases.

Some of the soil fungi have the ability to interfere with the growth of bacteria and other groups of microorganisms through the production of bacteriostatic and bactericidal substances. On the other hand, many fungi are greatly influenced by the growth of other microorganisms that produce fungistatic and fungicidal substances. In normal soils, a definite state of equilibrium is apparently established between the growth of fungi and other microorganisms.

Through their extensive vegetative mycelium in the soil, as well as through their metabolic products, fungi bind the finer soil particles, thus preventing their erosion from the soil.

Fungi are utilized as test agents for determining the nature and concentration of a variety of inorganic and organic compounds in the soil, ranging from available phosphorus and potassium to the vitamins thiamine and pyridoxine.

Through their varied physiology, soil fungi have been utilized industrially for the manu-

facture of organic acids, of diastatic, proteolytic, and pectolytic enzymes, of antibiotic agents, and of a number of other materials used in industry and in the home.

Although fungi form only a part of the soil population, their abundance, mass of growth, varied physiology, and many activities make them essential to numerous soil processes and, therefore, to the continued existence of life on this planet.

EPILOGUE

Fungi, comprising the filamentous, chiefly microscopic, nonchlorophyll-bearing plants, are widely distributed in nature. They occur abundantly in soil, water, and dust. They, together with the bacteria, are the universal scavengers, destroying the residues of plant and animal life. Although most of them are saprophytic, some are parasitic, capable of attacking living plant and animal tissues; still others are capable, through antagonistic properties, of repressing the growth of many microorganisms. Fungi affect the life of man in many ways and are, therefore, of great economic importance. An understanding of their control, where necessary, or their utilization, when desired, involves knowledge of their physiology and of their response to the environment and to the action of physical and chemical agents (118).

The investigations of the soil fungi carried out in the laboratories of the department of soil microbiology of the New Jersey Agricultural Experiment Station during the last three decades have touched upon many aspects of the ecology of the fungi, their physiology, their role in natural processes, especially in soils and composts, and their utilization. If to these are added the investigations of two other closely related groups of microorganisms, the actinomycetes and the bacteria, the former often spoken of as a group of fungi and the latter as fission fungi, the field of microbiology covered may be said to be fairly broad. These studies embraced a large number of problems, some limited in scope, others comprehensive in nature. The results obtained varied greatly in significance, some being merely exploratory in nature, and others involving extensive and detailed studies. Limited consideration given to certain problems was due in many instances to the departure of collaborators or assistants from the laboratory or to the lack of time and facilities to bring the problems to their proper conclusions. In other instances the methods and the knowledge of the field were not sufficiently advanced to justify more extensive work.

In these investigations, many collaborators from all corners of the earth have participated. Some forty of them have been listed as authors and co-authors, and the names of many others who have participated in the solution of some of these problems might have been added. To them, is due much of the credit for whatever positive results have been obtained in our efforts to solve the problem of the fungi and their importance in the cycle of life in nature, and especially in soil processes and in plant nutrition.

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PLATE 1

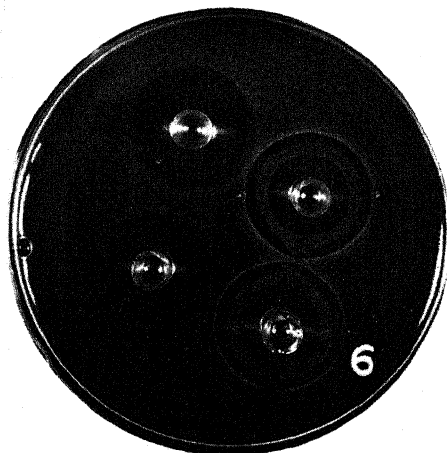
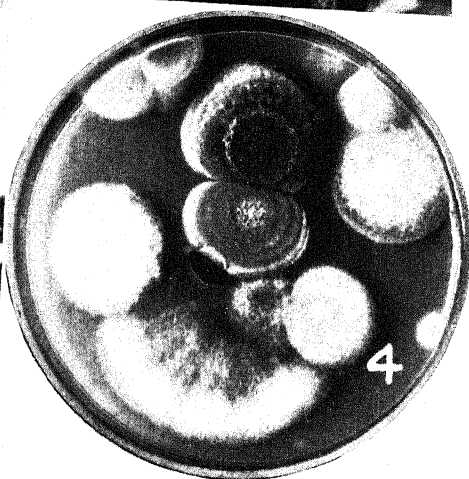
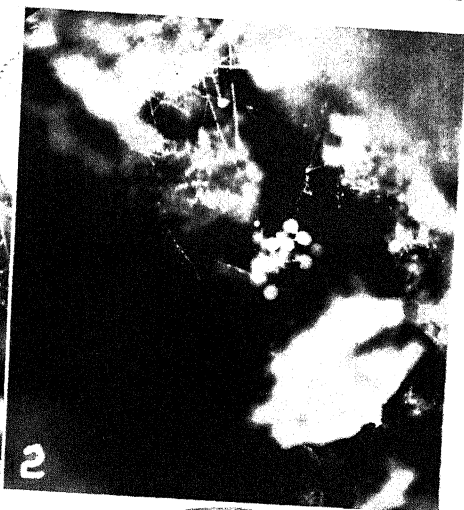
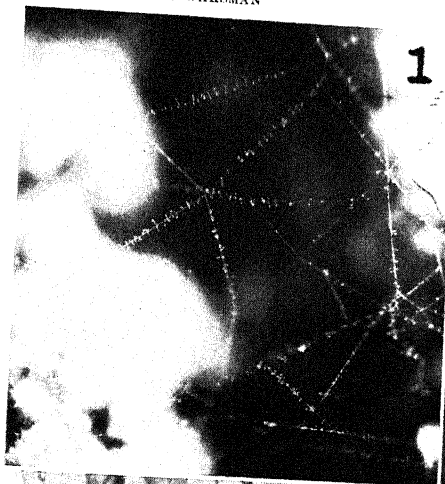
FIGS. 1 AND 2. Growth of fungi on bits of organic matter in soil. [From Kubiena and Renn (76).]

FIG. 3. Root hairs invaded by fungus hyphae and other organisms. [From Starkey (92).]

FIG. 4. Plate method for enumerating fungi, developed in our laboratory.

FIG. 5. Method of isolating fungi producing antibiotic substances.

FIG. 6. Antibacterial action of two types of substances produced by fungi.





WATER-DROP METHOD OF DETERMINING STABILITY OF SOIL STRUCTURE¹

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In order to determine the effect of microbiological and organic matter treatments on the resistance of soil structure groups or clods to the action of raindrops, it was necessary to devise some method of measuring this effect. This paper is designed to show the effect of various factors on the number or quantity of water drops required to disintegrate the structure of a unit of soil and the appropriate conditions for testing.

METHOD

Soils used

Subsoil from a deposit of typical Peorian loess was taken from a road cut near Plattsmouth, Nebraska, at a depth of 10 to 15 feet. It has 0.2 per cent oxidizable material as determined by the chromic-acid method, and its mechanical composition as determined by the hydrometer method is 14 per cent sand, 66 per cent silt, and 20 per cent clay. Marshall silty clay loam topsoil cultivated for many years at the Agronomy Farm, Lincoln, Nebraska, was used for comparison. The samples were prepared by breaking the air-dry soil into small lumps and then screening out units of desired size.

Laboratory procedure

A soil lump weighing approximately 0.15 gm. was placed on a 1-mm. screen, and drops of distilled water 4.7 mm. in diameter, falling 30 cm. from a burette, were allowed to strike it. When a soil lump or aggregate was broken down and at the point of being washed through the screen, it was considered destroyed.³ The end point was sharp for the loessial subsoil, but for the more highly aggregated Marshall topsoil the end point was more difficult to determine, because the lump frequently broke into several small aggregates that were kept together with a spatula until broken down. Three sets of determinations with 20 individual determinations in each were made for the data reported in this paper. Air-dry soil was used.

¹ Contribution by the Soil Conservation Service, U. S. Department of Agriculture, and the Department of agronomy, Nebraska Agricultural Experiment Station, Lincoln, Nebraska, cooperating. Journal Series No. 354.

² Associate bacteriologist, Soil Conservation Service. The writer is indebted to F. L. Duley and J. C. Russel, project supervisor and cooperative agent, respectively, Soil Conservation Service, for their suggestions during this investigation and in the preparation of this manuscript.

³ McCalla, T. M. 1942 The influence of biological products on soil structure and infiltration. *Proc. Soil Sci. Soc. Amer.* 7: 209-214.

RESULTS

Size of soil lump or aggregate

When soil lumps of loessial subsoil and Marshall topsoil varying in weight from 0.05 to 0.35 gm. were used, the number of water drops required to break down 0.1 gm. of soil decreased less per unit weight with lumps of 0.15 to 0.35 gm. than with smaller lumps, as shown in table 1. The Marshall soil required more drops to break down the structure than the loessial subsoil. It seemed probable that the smallest units of soil were not large enough to absorb the complete impact of the drop, therefore more drops were required per unit weight for the smaller lumps. There was less variation in drop requirements for large aggregates than for small. Hence 0.15 gm. was adopted as the standard size unit for testing.

TABLE 1

*Influence of soil lump size on number of water drops required to break down soil structure**

WEIGHT OF SOIL.....gm.	0.05	0.07	0.10	0.15	0.25	0.35
	Drops to destroy 0.1 gm. of soil					
Loessial subsoil (Peorian).....	8.8	7.1	6.1	4.7	4.3	3.8
Marshall topsoil.....	15.9	13.4	11.3	9.3	8.2	7.4

* Except where otherwise stated, the water drop size used in these tests was 4.7 mm. diameter falling from a height of 30 cm. at a rate of 1 drop per 4.5 seconds, and the weight of soil tested was 0.15 gm.

TABLE 2

Influence of fall distance of water drops on stability of soil structure

HEIGHT OF FALL.....cm.	5	30	60	80	150
	Drops to destroy 0.1 gm. of soil				
Loessial subsoil (Peorian).....	5.0	4.8	5.0	5.7	5.7
Marshall topsoil.....	11.1	9.1	8.8	8.6	8.9

Height of fall

When drops of water falling from heights varying from 5 to 150 cm. were allowed to strike lumps of loessial subsoil or Marshall topsoil, the number of drops required to break down the lumps was approximately the same for the different heights used, as shown in table 2. An increase in the height of fall from 5 to 30 cm. decreased slightly the number of drops required for the Marshall topsoil. For this reason, 30 cm. was selected as a desirable height for the drops to fall, and 4.7 mm. was used as the standard drop diameter.

The action of a water drop on soil structure seemed to be largely through the wetting and swelling of the soil, which loosened up the lump so that a drop could break it down. A dry lump of loessial subsoil required 984 gm. pressure to crush it, whereas only about 0.5 gm. of water was necessary to destroy the soil structure with falling water drops, or approximately 2000 times as much energy was re-

quired for the dry soil. This appears to be the reason why different heights of fall had little effect on the number of water drops required to break down the structure.

Intensity of drop application

Water drops were applied at rates varying from one drop per 0.55 second to one drop per 36 seconds to lumps of the two soils under study. No significant differences were found in the number of drops required to destroy the aggregates of the loessial subsoil due to rate of drop application. There was a significant increase with the Marshall topsoil, as shown in table 3. It is obvious that soil samples should be tested at the same rate of drop application. A rate of one drop per 4.5 seconds was selected because it gives sufficient time for counting the drops and does not extend the time of determination too long.

TABLE 3
Influence of water-drop intensity on stability of soil structure

ONE DROP PER NUMBER OF SECONDS.....	36	18	9	4.5	2.25	1.12	0.55
	Drops to destroy 0.1 gm. of soil						
Loessial subsoil (Peorian)	4.7	4.7	4.7	4.5	4.4	4.2	5.4
Marshall topsoil	7.5	7.8	8.8	9.7	10.8	11.9	15.4

TABLE 4
Influence of water temperature on number of water drops required to break down soil structure

TEMPERATURE°C.	0	28	60*
	Drops to destroy 0.1 gm. of soil		
Loessial subsoil (Peorian)	4.9	4.5	4.2
Marshall topsoil	11.4	9.7	8.7

* The temperature of the soil was 28°C.

Water and soil temperatures

The influence of water and soil temperature on the stability of the large soil aggregates or lumps was determined. Water and soil at 0° C., water and soil at 28° C., and water at 60° C. and soil at 28° C. were used. The higher the temperature of the water, the smaller was the number of drops required for aggregate disintegration, as shown in table 4. The effect of temperature, however, was less than might be expected, but was more marked in the Marshall soil than in the loessial subsoil. It would appear that slight variations in the room temperature of water or soil would not greatly influence the results.

Water-drop size

Decreasing the diameter of water drops from 4.7 mm. to 3.4 mm. and 2.4 mm. resulted in an increase in the number of drops but a decrease in the amount of

water required to break down the soil structure, as shown in table 5. The drop size of 4.7 mm. diameter was selected for most of these tests because this is the approximate size of drops delivered by the burettes used.

Moisture content of soils

Air-dry soil was compared with soil allowed to become wet by absorbing water for 15 minutes from saturated cheesecloth. A slightly smaller number of drops

TABLE 5
Influence of water-drop size on number required to destroy soil structure

DIAMETER OF WATER DROPS	mm.	4.7	3.4	2.4		
WEIGHT OF DROP	mgm.	54.4	20.6	7.2		
	Water to destroy 0.1 gm. of soil					
	<i>Drops</i>	<i>gm.</i>	<i>Drops</i>	<i>gm.</i>	<i>Drops</i>	<i>gm.</i>
Loessial subsoil (Peorian).....	4.5	0.24	6.8	0.14	11.7	0.08
Marshall topsoil.....	9.6	0.52	10.9	0.22	20.3	0.14

TABLE 6
Influence of moisture content of soil lump on number of water drops required to break down structure

MOISTURE CONDITION.....	WET	DRY
	Drops to destroy 0.1 gm. of soil	
Loessial subsoil (Peorian).....	4.1	4.4
Marshall topsoil.....	8.7	9.6

TABLE 7
Influence of soil treatment on number of water drops required to break down soil structure

SOIL USED.....	NUMBER OF DROPS PER 0.1 GM.
Loessial subsoil (Peorian).....	4.5
Loessial topsoil—virgin.....	29.5
Loessial subsoil (Peorian) plus 5 per cent sucrose—incubated 1 month.....	323.0
Marshall topsoil—cultivated.....	9.9
Marshall topsoil plus 4 per cent sucrose—incubated 2 days.....	296.0

was required to destroy the moist soil lumps, as shown in table 6. The differences were very small but sufficient to indicate that samples should be compared at similar moisture contents.

Effect of soil treatment

Different treatments were applied to the loessial subsoil and the Marshall topsoil, and these treated soils were then tested to determine the possibility of using the water-drop method for determining changes in soil structure. The results

show a wide range in the number of water drops required to break down the structure in soils having different treatments, which would indicate that the method may have value in detecting such differences (table 7).

Variation between determinations

There was considerable variation between the results of individual determinations, especially with highly aggregated soils. As a mean of 20 determinations, the standard deviation was 0.21 drop for the loessial subsoil requiring 4.5 drops of water per 0.1 gm. of air-dry soil to destroy the structure. For the Marshall topsoil requiring 9.7 drops of water per 0.1 gm. of soil to destroy the structure, the standard deviation was 1.6 drops.

DISCUSSION

By the method described it is possible to determine the influence of falling water drops on soil structure deterioration leading to the formation of the compact surface layer which forms on soil during rains. This compact layer forms somewhat gradually, however, and does not depend upon complete breakdown of structure. The method also affords a study of the action of water drops on the soil structure, as to how the large aggregate or lump disintegrates from the bombardment by water drops. The loessial subsoil seems to melt away under the impact of the water drops, much like sand, because it has little binding material to hold it together. The Marshall soil seems to break up instantly into smaller units of aggregates that eventually give way under the impact, or small aggregates are broken one by one from the larger unit as each drop strikes it.

In this procedure a unit of energy or hitting force is applied to a small lump of soil. Organic liquids that do not cause the soil to swell may be dropped on the soil almost indefinitely without destroying the structure. About 2000 times as much energy was required to crush a dry lump of soil as was necessary to break it down with water drops. The action of the falling water drop on soil structure is then largely through wetting and swelling, which loosens up the lump so that a drop can disintegrate the structure. The hitting action of the rain drop is necessary, however, for dispersing the soil sufficiently so that it finally results in the formation of the compact layer on soils during a rain.

SUMMARY

A method was devised for observing the effect of individual falling water drops on the stability of lumps or clods of soil. The number of water drops required to destroy a lump of soil increased with reduction of soil or water temperature, but decreased in a wet soil compared with a dry one. When the size of the drop was decreased, more water drops but a smaller quantity of water was required to destroy the structure.

A water-drop fall of 30 cm. and a soil lump size of 0.15 gm. were found satisfactory for the soils tested—Peorian loess subsoil and Marshall silty clay loam topsoil.

More variation in the number of drops required to destroy the soil structure was encountered with Marshall topsoil than with loessial subsoil.



THE TURMERIC DETERMINATION OF WATER-SOLUBLE BORON IN SOILS OF CITRUS ORCHARDS IN CALIFORNIA

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The relatively high boron content (11) of many soils and waters in southern California makes it most unlikely that any considerable area will be found deficient in boron. Nevertheless, there have been many avocado orchards, near citrus groves, in which boron applications have been made rather freely in order to avoid the effects of avocado tree decline. Studies (9) have not revealed, however, that avocado soils are in need of an increase in their boron content.

From extensive analyses of soils it has been concluded (18) that California is one of three large areas in the United States in which a boron deficiency is likely to be found. Rather striking responses to boron applications on Aiken soil in central California have been reported for olive trees (16), although no clear benefit from boron applications was observed in adjoining unthrifty orange trees. In certain areas in California apple trees have been shown (2) to respond to the use of boron.

Citrus trees penetrate the soil to various depths and have time in which to accumulate sufficient boron to meet their requirements. The present paper deals with the water-soluble boron found at various depths in citrus orchards of California. It also deals with improvements in the turmeric method for boron, by which minute amounts can be determined with considerable accuracy. Attention has been given to the factors that affect the soluble boron in soils: air-drying *vs.* oven-drying of soil samples, the changes in boron solubility with the long standing of cooled soil suspensions that previously had been heated, the effect of the temperature of cooling heated soil suspensions for filtration, the ignition of organic matter from filtered suspensions and the effect of ignition upon the recovery of boron added to such filtrates, and other factors such as dilution and pH variations.

METHOD

Investigations in regard to the water-soluble boron in soils have made use of spectrophotometric (10), titration (11), and recently, colorimetric (3, 6, 13) and biological (4) methods. The turmeric method (13) was chosen for the present investigation because of its simplicity and its accuracy in determining extremely small amounts of boron; in fact, the use of an A. C. model Fisher Electrophotometer permitted the determination of as little as 0.01 p.p.m. of boron, as shown in figure 1. Such refinement required careful checking of the details of the method.

Twenty unknown solutions could be determined in one day with the equipment

and routine described. A fresh suspension of calcium hydroxide was made by adding 0.925 gm. to 250 ml. of distilled water. A fresh turmeric suspension was made by adding 0.6 gm. of turmeric powder to 60 ml. of 95 per cent alcohol. Two sets, each consisting of 11 porcelain dishes, were cleaned and filled with distilled water, which was allowed to remain in the dishes until they were used.

Aliquots (usually 1 or more ml. but not exceeding 25 ml.) of the unknown solutions were pipetted into ten of the emptied dishes, while the eleventh served as the blank. Calcium hydroxide solution (usually 5 ml.) was added to each dish, which was then placed on a water bath. As each dish became dry it was at once removed from the bath. To each of the cool dishes at one time was added 1 ml. of a freshly prepared solution (5 ml. of concentrated HCl and 20 ml. of saturated oxalic acid solution) which was brought into full contact with the

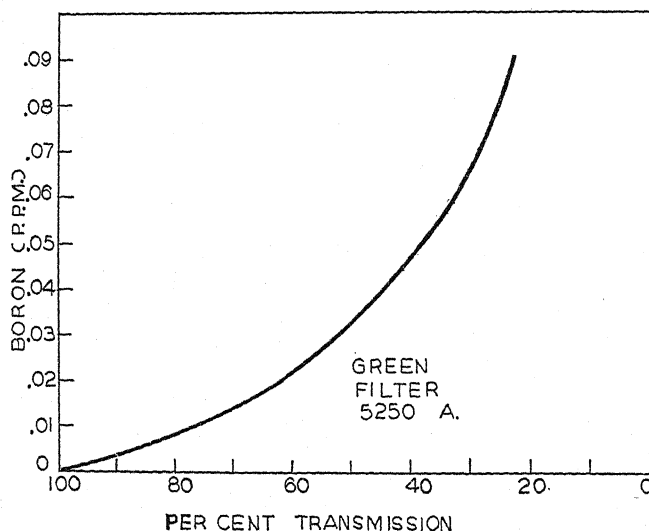


FIG. 1. CALIBRATION CURVE FOR THE STANDARD SOLUTION OF BORON: 0.0005 MGM. BORON IN 50 ML. FINAL VOLUME IS EQUIVALENT TO .01 P.P.M. BORON.

residue by rotating the dish. Then to each dish was added 2 ml. of the filtered suspension of turmeric in alcohol, and the dishes were again rotated, after which they were placed for 2 hours (usually 11:20 a.m. to 1:20 p.m.) on a second water bath maintained at 55°C.

Aliquots of other unknown solutions were added to the second set of dishes in the same manner as with the first set, the dishes being allowed to cool after the evaporation and to stand until 1:00 p.m. Then freshly prepared HCl-oxalic acid solution was added, the dishes were rotated, filtered alcoholic turmeric solution (saved in a stoppered flask as a left-over from the first set) was added, and finally the contents of the dishes were fully mixed by a second rotating of the dishes.

At 1:20 p.m. the first set of dishes was removed from the bath, and the second set of dishes was started on its 2-hour period of evaporation at 55°C.

To the first set of dishes that were cool was added some 95 per cent alcohol, and with the aid of a rubber policeman the colored solutions were passed through Whatman #42 filter papers, 9 cm. in diameter, into 50-ml. Pyrex volumetric flasks. The filter papers were washed several times with alcohol, and the flasks were brought to volume with alcohol. After being shaken, the alcoholic extract of the developed colors were run successively into the 23-ml. cylindrical ($\frac{7}{8}$ inch diameter) absorption cell, which was placed in an A.C. model Fisher Electrophotometer. The percentage of light transmission was then determined with the use of a green filter (5250 Å.). From an enlarged graph that showed the relation of the percentage of light transmission plotted against the parts per million of boron (fig. 1), the boron content of the aliquot was found and that of the unknown solution was calculated.

At 3:20 p.m. the second set of dishes was removed from the bath and subsequently treated similarly to the first set.

PREPARATION OF THE CALIBRATION GRAPH

Dissolve 0.5716 gm. of dry boric acid in 1000 ml. of distilled water. This solution contained 0.1 mgm. of boron per milliliter and was stock solution A. Diluting 50 ml. of stock solution A to 500 ml. with distilled water produced stock solution B, which contained 0.01 mgm. of boron per milliliter. A third stock solution C containing 0.001 mgm. per milliliter was prepared by diluting 50 ml. of stock solution B to 500 ml. with distilled water. Various amounts of stock solution C were used as the unknown solutions in preparing the graph shown in figure 1.

MATERIALS AND EQUIPMENT

A good grade of porcelain dishes (marked with a blue arrow) $1\frac{5}{8}$ inches high, $3\frac{1}{2}$ inches wide, and of 75 ml. capacity was used. For determinations involving ignition at low heat, vitreosil casseroles (without handles) $1\frac{1}{2}$ inches high, 3 inches wide, and of 75 ml. capacity were used.

At the end of a day's use, the dishes were washed successively with tap water, dilute HCl, and tap water, and then were dipped into concentrated H_2SO_4 and stacked in a glass dish. Before the determinations were made, the dishes were washed with tap water and then distilled water and were allowed to remain filled with distilled water until just before the aliquots of the unknowns were to be pipetted.

A water bath heated with gas was available for evaporation of the unknown solutions, a blank determination being a part of every set. As unavoidable delay would accompany the dropping of the temperature of this bath to 55°C . a second water bath ($11\frac{1}{2}$ inches wide, $26\frac{1}{2}$ inches long, and $3\frac{1}{2}$ inches deep, with 12 holes each 3 inches in diameter) was used for the development of the color. This bath was placed on a piece of asbestos over a two-burner gas range, which enabled rapid heating of the bath. Distilled water was used in both baths. When the temperature of the second water bath reached about 52° to 54°C ., the gas was shut off, and the water was heated electrically to constant temperature at 55°C . as follows: Through a corner hole in the bath a knife-type heater (250

watt) was inserted and slanted in order to place the heating element under water. A motor stirrer was placed directly above this same hole in the bath and served to keep the water circulating. A cylinder made of cardboard was placed over the hole and about the stirrer to prevent the spattering of oil or water into the dishes. A slight cut was made through the rim of the corner hole at the other end of the bath, into which offset was placed a De Khotinsky bimetallic thermoregulator equipped with a condenser and a neon-filled pilot lamp. This hole was also used to hold one of the dishes. A thermometer was used for reading the temperature of the bath. Such a temperature control was desirable even though tests showed that no appreciable deviations in the results occurred when the temperature of the bath was maintained at 52°, 55° or 58°C. Sufficient water to touch the evaporation dishes was kept in the bath. The results were not reliable when the temperature of the bath was not well controlled or when the bath was not kept filled with water. Comparisons of the colors of the residues obtained at higher temperatures gave inconsistent results. A period of 2 hours was used for the color development (evaporation at 55°C.), and enabled the use of two sets of dishes, each consisting of ten unknowns and a blank, per day. The blank was most useful in indicating the reliability of the results as well as for making correction allowances in the color readings. The importance of the control of temperature during the development of color in the determination of boron with the quinalizarin procedure has been pointed out by previous investigators (14).

Kavalier glass flasks were used for solutions involved in the color development. The bottle of powdered calcium hydroxide was of c.p. grade (Cenco lot 1102) and was thoroughly shaken when used for the first time. An inverted paper bag was used to cover the bottle to protect it from dust. The turmeric powder (A. H. Thomas) was likewise mixed and protected. Suspensions of these in water and in alcohol respectively, if prepared when the day's work is begun, are suitable for use later in the morning when they are needed. It was considered unnecessary to wash the turmeric powder with distilled water before using it for alcoholic suspensions (8), because the blanks showed no improvement.

The HCl used was c.p. Baker's analyzed grade (lots 11542 and 1.2141) each source of which was satisfactory. The oxalic acid was Baker's c.p. special grade and was heated in a Kavalier flask with distilled water to near saturation and was then cooled. After the solution was poured off, more water was added, and the recrystallization was repeated. Such a product was most satisfactory.

IMPORTANCE OF CERTAIN DETAILS IN THE METHOD

Some investigators (1, 12) have discarded the turmeric method in favor of the quinalizarin method or have found the former less satisfactory. It is important therefore to note the difficulties that were experienced before satisfactory results could be obtained.

Redistilled water was used at first but the quantity required and its quality, due to lack of Kavalier glass parts, did not warrant continuance of its use. Dis-

tilled water of high grade was obtained, without redistillation, from the large gas still in which softener-treated water is distilled for the entire station at Riverside. The still was allowed to operate for about 15 minutes before the water was taken. The water was collected in large Kavalier flasks as it came from the condenser. Regular distilled water taken from the large storage tanks was used for washings of no great importance, and the specially collected distilled water was used for final rinsings and other purposes as necessary.

The principle was adhered to that all solutions or chemicals involved in the production of the colored residue should be as nearly boron-free as possible. This saved much unnecessary precaution in the treatment of the residue. For example, use of Pyrex 50-ml. volumetric flasks, of 95 per cent alcohol that was redistilled after each day's use, and of the same rewashed filter papers weeks at a time for removing the solids in the alcoholic extraction of the color, involved factors subsequent to development of the color residue and therefore required no special precautions.

In any part of the method that is involved in the color development, however, every care must be exercised. For example, the 95 per cent alcohol used in the turmeric suspension must be boron-free. The commercial 95 per cent alcohol was obtained from an iron or steel drum, and 5 gallons was placed in a Pyrex bottle in order to avoid oxidizing or reducing agents (15). Immediate distillation, with or without the addition of c.p. calcium oxide, into Kavalier flasks gave a satisfactory reagent. On the other hand, if the original commercial alcohol was stored in the Pyrex bottle for prolonged periods, the distilled product was unsatisfactory, and the more so the longer the previous storage had been in Pyrex. It was realized that boron would be dissolved out of the Pyrex glass into the commercial alcohol, but no reference thus far has been noted that boron in appreciable amounts may come over with the alcohol upon redistillation, even in the presence of lime. A 3-liter flask of 95 per cent alcohol freshly obtained from the drum was heated and after the first that came over was discarded, the remainder of the distillate was satisfactory. When boron was added to the contents of the distilling flask, however, the distillate was heavily contaminated with boron, and with continued distillation the product remained unsatisfactory even after lime was added to the distilling flask. Although the method of distilling boron with methyl alcohol is well known, no reference to boron distillation with ethyl alcohol had come to the author's attention.

Another important matter is the quality of the paper used in filtering the alcoholic turmeric suspension. A Whatman #42 paper, 9 cm. in diameter, from a box with a light brown paper seal and with a declared ash content of 0.057 mgm. per circle was found to be satisfactory. With the same kind of paper from another box but with a red paper seal and a declared ash content of 0.064 mgm. per circle, very unsatisfactory results were obtained. With the turmeric suspension filtered through the first paper, the customary blank gave roughly 90 per cent light transmission, whereas with the second paper the value was roughly only 77 per cent. The possibility exists that this second paper

contains boron, sulfites, or some other oxidizing or reducing substance. When the better paper was used, no further difficulties were encountered.

DETERMINATION OF WATER-SOLUBLE BORON

The usual procedure was to place 20 gm. of air-dried soil (passed through a sieve with a mesh 1 mm. in diameter) in a 300-ml. Kavalier glass Erlenmeyer flask, add 40 ml. of distilled water, connect the flask with a reflux condenser, boil for 5 minutes, then stopper lightly, and cool as required. When filtered with suction through a Büchner funnel using a circle of Whatman #42 paper, 7 cm. in diameter, the filtrate at first was usually cloudy but soon became clear. Instead of being inserted into a glass tube in a suction flask (6), the funnel was placed through the stopper of a conical-shaped separatory flask bearing a capillary side tube near the top, and the outlet of this separatory flask in turn was inserted through the stopper of the suction flask. Suction was applied to both flasks. A piece of rubber tubing with a pointed tip was attached to the funnel. Cloudy solution that entered the separatory flask did not contact the glass except just above the stopcock and was removed at intervals into the suction flask by turning the stopcock. Soon a clear solution was obtained with a minimum of loss and was finally transferred to a Kavalier flask by detaching the suction flask and then turning the stopcock after closing the vacuum valve.

When 20 gm. of soil was used with 20 ml. instead of 40 ml. of distilled water, a Gooch crucible containing a small circle of Whatman #42 filter paper was used instead of the Büchner funnel. The crucible was placed in a rubber ring on the rim of a glass funnel that was inserted into the top of the separatory or filter flask. A rubber tube, with pointed tip, was attached to the stem of the funnel. After the cloudiness of the filtrate ceased, the funnel and flask were cleaned, and the clear solution was collected with little loss.

EFFECT OF IGNITION ON BORON DETERMINATION AND RECOVERY OF ADDED BORON

Filtered solutions were made of refluxed suspensions of soil (20 gm. air-dried soil in 40 ml. distilled water), and the boron content was determined with and without the ignition of the organic matter. To each vitreosil casserole (with handle removed) in which the aliquot of the unknown solution was evaporated, was added 5 ml. of the calcium hydroxide suspension. Its addition to prevent the loss of boron during ashing was not found to be necessary by previous investigators (12), but it was convenient to have the calcium present because, in acidifying the contents of the dish with the oxalic-HCl solution, the effervescence was a visible aid in making contact with the contents of the entire dish.

It was essential to learn whether the ignition was accompanied by any loss of boron. Fisher burners were used without air entering the vents. Determinations of boron with ignition of the evaporated aliquot gave satisfactory values in most cases (table 1). When known and very small amounts of boron were added to the aliquots prior to the evaporation and ignition, recovery of the added boron was very satisfactory.

VARIOUS FACTORS AFFECTING WATER-SOLUBLE BORON

Effect of oven-drying soil samples and of long standing of suspensions in contact with soil

A group of eight soils were selected from among a large number of collected citrus soil samples. As shown in table 2, considerably more boron was brought into solution at 65°C. than at room temperature. A delay of 24 hours in filtering heated soil suspensions did not reduce the boron content of the filtrates of the heated suspensions to the level of the unheated ones (7). In some cases the

TABLE 1

Effect of ignition on the boron content (air-dry soil basis) of filtered soil suspensions and on the recovery of added boron

SOLUTION SAMPLE	BORON CONTENT		SOLUTION SAMPLE	BORON CONTENT WITHOUT ADDED BORON	BORON ADDED	BORON RECOVERED
	No ignition	Ignition				
<i>ml.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>ml.</i>	<i>p.p.m.</i>	<i>mgm.</i>	<i>mgm.</i>
5	0.35	4	0.363	0.0015	0.00158
5	0.35	0.35				
7	0.31	0.34	6	0.336	0.001	0.00079
5	0.35	6	0.0015	0.00154
7	0.33	0.34	6	0.002	0.00192
6	0.27	0.26	5	1.825	0.002	0.002
5	0.29	0.24				
			3	0.373	0.0015	0.00147
10	0.33				
5	0.34	6	0.345	0.001	0.0012
9	0.31	6	0.0015	0.00168
5	0.30	0.30	10	0.370	0.001	0.00109
6	0.31	0.30				
7	0.29	0.29				
5	0.30				
15	0.28				
6	0.30	0.24				
5	0.29				
5	0.30				

heating of air-dried soils or of rewetted air-dried soils that were again air-dried, caused little change in the water-soluble boron whereas in others considerable change occurred.

Effect of degree of cooling before filtration

The suggestion sometimes is made that clarification may be facilitated by working with a warm solution. The refluxed soil suspensions used in table 3 were cooled to various temperatures before filtration. The degree of cooling

TABLE 2
Soluble boron (air-dry soil basis) in soil suspensions
20 gm. of air-dry soil in 40 ml. distilled water

LOCATION	SOIL TYPE	DEPTH OF SOIL SAMPLE	SOLUBLE BORON CONTENT					
			Air-dry soil		Air-dry soil heated at 100°C. for 2 days and then air-dried		Re-wetted air-dry soil (30 cc. distilled water and 100 gm. air-dry soil) dried at 100°C. for 2 days and then air-dried	
			Suspension at 65°C. for 16 hours followed by 24 hours at laboratory temperature	Suspension 40 hours at laboratory temperature	Suspension at 65°C. for 16 hours followed by 24 hours at laboratory temperature	Suspension 40 hours at laboratory temperature	Suspension at 65°C. for 16 hours followed by 24 hours at laboratory temperature	Suspension 40 hours at laboratory temperature
		<i>feet</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Oxnard.....	Yolo loam	0-1	1.59	1.00	1.92	2.09	1.36
Tustin.....	Yolo loam	2-3	1.38	0.84	1.32	0.76	1.28	0.68
Tustin.....	Yolo loam	1-2	0.94	0.55	0.94	0.51	0.98	0.56
Santa Ana....	Yolo loam	2-3	1.60	0.99	1.69	0.93	1.62	0.90
Santa Ana....	Yolo loam	1-2	1.18	0.64	1.08	0.55	1.11	0.56
W. Ontario..	Hanford fine sandy loam	1-2	0.57	0.36	0.44	0.34	0.39	0.35
Santa Paula.	Yolo sandy loam	1-2	1.91	0.92	1.73	0.92	1.57	0.97
Riverside....	Hanford loam	0-2	0.31	0.17	0.35	0.20	0.44	0.19

TABLE 3
Soluble boron in refluxed soil suspensions when cooled to various temperatures before filtration
20 gm. of air-dry soil in 40 ml. distilled water

LOCATION	SOIL TYPE	DEPTH OF SOIL SAMPLE	WATER-SOLUBLE BORON (AIR-DRY SOIL BASIS); SOIL SUSPENSION REFLUXED 5 MINUTES, THEN COOLED IN BATH AT TEMPERATURE INDICATED AND FILTERED			
			100°C.	60°C.	40°C.	20°C.
		<i>feet</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Citrus Exp. Sta.....	Hanford loam	0-1	0.48	0.43	0.43	0.41
Santa Paula.....	Yolo sandy loam	1-2	3.54	3.02	2.50	2.39
Santa Ana.....	Yolo loam	1-2	1.51	1.27	1.20	1.24
W. Ontario.....	Hanford fine sandy loam	1-2	0.82	0.95	0.80	0.72
Tustin.....	Yolo loam	1-2	1.43	1.12	1.11	0.96
Santa Ana.....	Yolo loam	2-3	2.87	1.90	1.80	2.13
Oxnard.....	Yolo loam	0-1	2.18	1.86	1.98	1.72
Tustin.....	Yolo loam	2-3	2.23	1.55	1.72	1.26

before filtration has a varying effect on the water-soluble boron depending on the particular soil. In some cases the cooling temperature shows but little effect, whereas in others it is pronounced.

Effect of dilution and of pH

Samples of soil were obtained, with one exception, from various citrus orchards and, after being air-dried, were passed through a sieve with mesh 1 mm. in diameter. In each case, 20 gm. of soil was used, and the distilled water additions were 20, 40, 80, 100, 120, and 160 ml. The soil suspensions were refluxed at boiling temperature for 5 minutes and were cooled to room temperature before filtration.

Sample 8 was obtained from a pasture near the Citrus Experiment Station. The first ten soil samples then, with the exception of soil 8, are representative of the soils in excellent orchards. In contrast, sample 11 represents the upper 16 inches of soil taken from an unthrifty navel orange orchard near Oroville and close to olive trees that responded to applications of boron to the soil (16). The citrus trees (16), however, have not as yet responded to the boron applications.

TABLE 4

Water-soluble boron in soils (air-dry soil basis) at various dilutions with distilled water

Soil No.	WATER-SOLUBLE BORON CONTENT (P.P.M.) WHEN VARIOUS AMOUNTS OF DISTILLED WATER (ML.) WERE USED WITH 20 GM. OF AIR-DRIED SOIL					
	20 ml.	40 ml.	80 ml.	100 ml.	120 ml.	160 ml.
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Soil 1	0.66	1.11	1.50	1.51	1.55	1.91
2	0.77	1.37	1.72	1.76	1.94	2.07
3	0.43	0.38	0.39	0.51	0.47	0.58
4	0.50	0.74	0.94	1.05	1.00	1.17
5	0.94	1.71	2.17	2.34	3.00	2.97
6	0.64	1.38	1.93	2.15	2.35	2.59
7	0.49	0.76	1.15	1.05	1.20	1.38
8	0.22	0.28	0.37	0.34	0.39	0.40
9	1.57	1.74	2.00	2.13	2.18	2.40
10	1.94	2.73	3.50	4.19	3.80	4.14
11	0.08	0.10	0.15	0.18	0.18	0.19

From the data in table 4 it appears that as the dilution increases the water-soluble boron (air-dry soil basis) increases. The generally large increase in the water-soluble boron content as the dilution increases from 1:1 to 1:2 (soil-water ratio), points the way for further investigations with moisture contents approaching those found under field conditions.

When 20 gm. of soil sample 11 was refluxed 5 minutes at the boiling temperature with 40 ml. of HCl (pH 3.0), the soluble boron (air-dry soil basis) was 0.11 p.p.m. as compared with values of 0.10, 0.13, and 0.16 p.p.m. when distilled water was used with various samples of this soil. The filtered acid solution had a pH of 5.73. When HCl (pH 1.1) was used, the pH of the filtered solution was 2.08 and the soluble boron was 0.07 p.p.m.

A sample was obtained in a nearby orchard that responded to the application of boron to the soil. With 20 gm. of soil in 40 ml. of acid with the usual refluxing, cooling, and filtering, the following results were obtained: with HCl (pH 3.0)

the filtered solution showed a pH of 5.64 and a boron content (air-dry soil basis) of 0.08 p.p.m.; with HCl (pH 1.1) the pH of the extract was 2.14 and the boron content on the same basis was 0.07 p.p.m. The boron values obtained when distilled water was used were 0.12 and 0.14 p.p.m. respectively with two samples of soil. These values, for the orange as well as for the olive soil, showed a very low soluble boron content even when acid was used. These results are of interest because other investigators (18) have reported that if a soil is low in acid-soluble boron it is likely to be deficient in boron. A 1 per cent HCl solution was reported to extract one and one half to two and one half times as much boron from soil as did water alone (19).

According to these studies with acids, the citrus trees in question should benefit from applications of boron, although no such benefit as yet has been evident (16). It is possible that later some benefit may occur or that some other factor is preventing a response to the boron. If these citrus trees are not deficient in boron they approach such a condition, for navel orange leaves obtained¹ June 25 from a tree in the untreated soil contained 9.4 p.p.m. water-soluble boron (dry-weight basis) and 12.5 p.p.m. water-insoluble boron, whereas another leaf sample obtained December 28 contained 3.8 p.p.m. water-soluble and 13.0 p.p.m. water-insoluble boron. Healthy orange leaves at Riverside contained 29 p.p.m. water-soluble and 14 p.p.m. water-insoluble boron. When 4 ounces of borax (applied February 19 of the year in which the leaf sample was obtained) was applied to the soil about a tree near the untreated tree, the leaves of June 25 contained 76.7 p.p.m. water-soluble and 12.8 p.p.m. water-insoluble boron. When 8 ounces of borax was applied to the soil about a tree in December (1 year prior to the leaf sampling) the leaves contained 133.8 p.p.m. water-soluble and 17.6 p.p.m. water-insoluble boron. Leaf symptoms in citrus do not seem to become evident until the water-soluble boron reaches a very low value.

Not every citrus soil² in Butte County, where olives respond to boron applications to the soil, is low in water-soluble boron. In a 40-year-old navel orange orchard on Aiken clay loam near Wyandotte, the water-soluble boron content of the soil (air-dry soil basis) was as follows: 0 to 6 inches, 4.72 p.p.m.; 6 to 12 inches, 2.97 p.p.m.; 12 to 24 inches, 2.10 p.p.m.; 24 to 36 inches, 1.78 p.p.m. respectively. In a 30-year-old navel orange orchard on Redding gravelly loam near Thermalito, the water-soluble boron content of the soil on a similar basis was: 0-6 inches, 2.78 p.p.m.; 6-12 inches, 2.37 p.p.m.; 12-24 inches, 2.10 p.p.m.; and 24-30 inches, 3.28 p.p.m. respectively.

One soil in a declining avocado orchard was used in a test of the effectiveness of acid in setting boron free. With 20 gm. of soil, from a depth of 0-12 inches, in 40 ml. HCl (pH 3.0) and treated as usual, the filtered extract showed a pH of 5.91 and 0.28 p.p.m. of soluble boron as compared with 0.28 p.p.m. when distilled water was used; when HCl (pH 1.1) was used, the filtrate had a pH of 1.85 and contained 0.14 p.p.m. of soluble boron. Similarly for soil from the 12 to

¹ Soil and leaf collections were made through the kindness of C. E. Scott and H. P. Everett.

² Through the kindness of H. P. Everett, farm advisor for Butte County.

24 inch. depth: with HCl (pH 3.0) the filtrate had a pH of 6.32 and contained 0.37 p.p.m. of boron (air-dry soil basis) as compared with 0.46 p.p.m. when distilled water was used; with HCl (pH 1.1) the values were pH 2.48 and 0.34 p.p.m. In this soil, which was heavy and very nearly impervious, an increased acidity failed to increase the soluble boron (air-dry soil basis). No boron-deficiency symptoms were evident in the tree growth, although the water-soluble boron content of the dry matter of the leaves was 2.36 p.p.m. and the water-insoluble content 11.88 p.p.m., both relatively low values for avocado leaves.

The use of sulfur on Yolo loam in a Valencia orange orchard near Tustin in Orange County should be referred to because of its bearing on water-soluble boron. Ten years ago in this large orchard, three rows of trees were selected and in all three rows, beginning at one side of the orchard, sulfur was applied to the soil in the tree square. The first third of the trees in the rows received sulfur at the rate of 60 pounds applied in two lots to the soil of each tree square. By the same procedure, the second third received 80 pounds, and the last third

TABLE 5
pH values and water-soluble boron content of citrus soil

SULFUR APPLIED TO THE SOIL (TREE SQUARE)	DEPTH OF SOIL SAMPLE	MOISTURE PER- CENTAGE OF SOIL (AIR-DRY SOIL BASIS) AT TIME OF SAMPLING	pH AT THE FIELD MOISTURE CONTENT	pH AT 1 to 5 SOIL-WATER RATIO	WATER-SOLUBLE BORON CONTENT (AIR-DRY SOIL BASIS)
<i>pounds</i>	<i>feet</i>	<i>per cent</i>	<i>pH</i>	<i>pH</i>	<i>p.p.m.</i>
0	0-1	23.9	6.97	8.25	1.99
	1-2	24.8	7.10	8.82	1.06
	2-3	24.2	7.18	8.92	0.63
100	0-1	17.9	6.90	8.31	4.26
	1-2	20.6	7.17	8.16	2.25
	2-3	22.9	6.98	8.51	0.61

received 100 pounds of sulfur per tree square. Ten years after the applications were made, the trees in the three rows tower above the remainder of the orchard, whatever the factors involved may be. Soil samples taken 10 years after the treatment was applied, show, as seen in table 5, very little difference in the pH values at the field moisture content, whereas at the 1 to 5 soil-water ratio the pH values show less alkalinity below the first foot of soil where sulfur had been applied. The water-soluble boron contents were slightly more than double the values for the untreated soil at comparable depths down to the third foot, in which the values were practically identical in the treated and untreated soil.

Changes in soluble boron content on standing

Three soils were used to determine whether the soluble boron content changed upon long standing of the suspension in contact with the soil. Twenty grams of soil and 40 ml. of distilled water were refluxed at boiling temperature for 5 minutes. When cool, the first suspension was filtered and showed 1.74 p.p.m. water-

soluble boron (air-dry soil basis). A similar test, in which thymol was added when the suspension was cool, showed a water-soluble boron content of 1.65 p.p.m (air-dry soil basis) when the suspension was allowed to remain unfiltered for 3

TABLE 6
Water-soluble boron in soils of citrus orchards
Boron in p.p.m., air-dry soil basis. Soil samples taken at 1-foot depth intervals*

1	2	3	4	5	6	7	8	9	10	11
1.43	0.63	0.75	1.02	1.42	1.60	2.38	5.03	2.67	5.31	5.89
1.14	0.33	0.96	0.44	0.77	1.05	1.35	3.34	0.94	7.98	10.73
0.84	0.25	1.88	0.48	2.20	2.65	0.85	2.84	1.37	4.94	5.24
0.65	1.38	3.44	0.55	1.24	2.67	1.77	4.94	2.19	2.84	4.53
0.55	1.31	1.14	2.22	0.69	2.39	1.45	2.09	1.63	7.40	5.34
0.38	0.94	1.94	1.46	0.84	2.06	0.95	2.68	1.28	7.37	3.26
0.38	1.58	2.26	1.34	1.47	1.39	1.80	0.99	1.76	5.40	5.94
1.41	1.07	2.34	1.61	1.28	1.47	0.49	1.69	0.78	6.96	3.98
1.20	0.94	1.76	1.53	1.08	1.37	0.38	3.13	0.51	4.34	7.12
1.17	1.98	2.78	3.58	1.25	0.53	0.56	1.66	0.57	3.58	5.19
1.28	1.16	3.00	1.72	0.81	1.28	0.42	0.81	0.50	2.77	8.42
0.94	0.63	3.31	2.19	1.13	0.98	2.16	1.69	3.96	3.55	4.18
0.93	0.66	1.78	1.45	0.85	1.79	0.96	2.00	2.96	6.25	9.75
1.31	0.58	2.90	3.25	1.11	1.14	1.99	1.19	4.08	3.16	6.16
1.31	0.50	2.91	1.75	2.78	3.58	1.64	2.00	4.65	2.74	4.38
0.31	0.48	4.96	2.34	0.94	1.39	1.27	2.47	3.13	7.47	4.71
2.26	0.65	1.48	1.63	2.50	1.47	0.94	1.65	3.38	3.44
1.84	0.45	1.48	3.39	0.60	2.31	1.12	0.79	1.84	3.41	3.63
1.55	1.07	1.61	2.88	1.60	0.76	1.73	1.40	1.52	3.83	3.31
1.29	1.07	1.48	1.13	0.65	2.38	0.80	1.07	1.94	4.18	2.50
0.85	0.41	1.51	1.25	1.27	2.94	1.33	0.61	2.23	5.92	3.51
2.09	0.32	1.80	1.88	1.38	2.20	1.76	0.83	1.69	5.98	3.45
1.30	1.27		2.40	0.31	1.68	0.95	0.55	2.72	2.84	4.17
0.90	0.53		1.30	0.93	1.50	0.56	2.06	3.56	4.03	3.28
0.88	0.41		1.92	0.87	2.78	1.38	0.51	2.63	3.58	3.96
1.16	0.71		2.59	0.88	1.24	0.93	2.96	3.42	3.78	4.43
0.96	0.55		3.19	0.52	1.51	0.50	1.13	1.86	2.75	
0.68	0.50		1.76	0.56	1.69	0.77	0.93	2.95	3.75	
2.52	0.86		1.64	1.64	1.76	1.19	1.05	3.19	5.54	
1.92	0.83		0.68	0.53	1.28	0.75	0.72	2.75	4.40	
1.81	0.66		0.98	1.55	1.05	1.50	2.76	0.98	7.42	
	0.56		2.27	0.83	2.39	1.46	1.48	0.95	3.89	
			0.58	0.88	1.00	1.43	1.40	0.86	5.73	
			0.98	1.63	1.37	4.69	2.51	1.55	4.88	
			1.15	2.69	1.28	1.11	1.71	3.45	4.38	
			1.19	1.69	1.39	1.01	1.28	4.17	5.50	
			0.73	2.75	0.25	1.50	3.32	3.28	7.40	
			0.84	3.19	0.48	1.36	3.96	4.45	
				3.34	0.36	1.17	1.26	4.43	4.26	
				2.89	1.24	0.82	0.96		3.63	
				1.94	0.45	0.76	3.29		7.50	
					0.42	0.95	1.46		9.65	
					0.74				3.94	
									4.00	

* $\frac{1}{2}$ -foot depth intervals designated by vertical lines.

days. The second soil showed 2.73 p.p.m. when filtered upon cooling; with thymol added and the suspension left unfiltered for 3 days, the soluble boron was 2.84 p.p.m. on a similar basis. The values for the third soil were 0.76 and 0.65 p.p.m. respectively when filtered upon cooling and after standing unfiltered

for 3 days. The filtered thymol-containing solutions after standing 4 more days showed 1.60, 2.64, and 0.64 p.p.m. respectively on the usual basis. Thus no striking changes took place when the solutions were left standing in contact with the soil after refluxing, provided that the action of organisms was excluded.

A large number of boron determinations were made upon filtrates, portions of which were tested directly after filtration following the cooling to room temperature, whereas other portions were tested after standing in stoppered flasks for several days, with and without thymol. Without thymol in the cooled suspension, many of the filtrates decreased in boron content or remained steady; with thymol, the values remained steady. Though the solubility of the boron may decrease (7) when the soil is allowed to remain for some time in contact with the solution, it appears likely that organisms may be largely responsible for the changes.

Water-soluble boron in citrus soils

Samples of soil at various depths were obtained in representative orchards in the principal citrus areas of southern California. Most of the soils (columns 1-9 inclusive, table 6) were air-dried and passed through a sieve with mesh 1 mm. in diameter, and a few (columns 10 and 11, table 6) were dried at 100°C. for 2 days before being sieved (see table 2). The suspension, consisting of 20 gm. of soil in 40 ml. of distilled water, was refluxed at boiling temperature for 5 minutes and cooled to room temperature before filtration. The turmeric method was used to determine the boron, which was calculated on an air-dry soil basis.

Table 6 shows the water-soluble boron in the soils. The data in the first two columns are for orchard soils in which the water-soluble boron decreases with increasing soil depths. In the third column are the soils in which the water-soluble boron increases with increasing depths. In columns 4 to 9 inclusive, are the data that show no particular trend with changing soil depths. The data in columns 10 and 11 are for soils from areas particularly high in boron and in which growth difficulties are often manifold. These soils were collected at a considerable distance from the laboratory, and though drying them by heating shortly after sampling may have induced certain changes in their relationships, these changes probably were no greater changes than would have occurred had the samples remained undried for long periods.

The data in table 6 give some notion regarding the range of water-soluble boron encountered in citrus soils in California. Water-soluble boron in Georgia soils ranged from 0.01 to 0.65 p.p.m., and in Illinois soils from 0.20 to 1.22 p.p.m. (6). The water-soluble boron in Hawaiian soils (17) decreased with increasing depths, and ranged from 0.4 to 3.2 p.p.m., the surface soils containing at least twice as much boron as the corresponding subsoils (5).

SUMMARY

Certain details of the turmeric method for boron determination were examined in order to ascertain why the method, which is accurate for very small amounts of boron, has not given greater satisfaction when used by some investigators.

All solutions, chemicals, or materials involved in the production of the colored residue, must be as nearly boron-free as possible. No such requirements are involved in the subsequent preparation of this residue for photometric measurement. The purity of the alcohol for the turmeric suspension and the quality of the paper for its filtration (unless centrifuging is used) require special attention. Satisfactory results were obtained when the temperature of the bath used for obtaining the colored residue was electrically controlled and the period for evaporation made comparable in each case. The importance of including a blank with every set of unknowns is pointed out.

Clear filtrates of cool soil suspensions were readily obtained without rewarming the suspensions. Ignition of the organic matter in filtered soil suspensions was carried on at low temperatures without appreciable loss of boron and did not interfere with the satisfactory recovery of small amounts of added boron.

The heating of soil suspensions brought into solution more boron than that found in unheated suspensions kept for a similar period. The long standing of suspensions heated then cooled did not lower the soluble boron to the level of that of unheated suspensions.

The oven-drying of air-dried soils or of rewetted air-dried soils that were again air-dried, caused little change in the water-soluble boron content in some cases and considerable change in others.

The degree of cooling of heated soil suspensions before filtration, in some cases, materially affected the water-soluble boron values obtained.

As dilution in the soil suspensions increased, the water-soluble boron (air-dry soil basis) increased. This indicates the need of additional investigation of the soluble boron at field moisture percentages.

The application of sulfur to orchard soil resulted in increased water-soluble boron even after a lapse of 10 years.

An Aiken soil from olive and citrus areas near Oroville, showed no increased boron solubility when acid was used instead of distilled water in making the soil suspensions, and yet the olive trees alone have thus far responded to the application of boron to the soil. Other citrus soils near Oroville were found to contain large amounts of water-soluble boron.

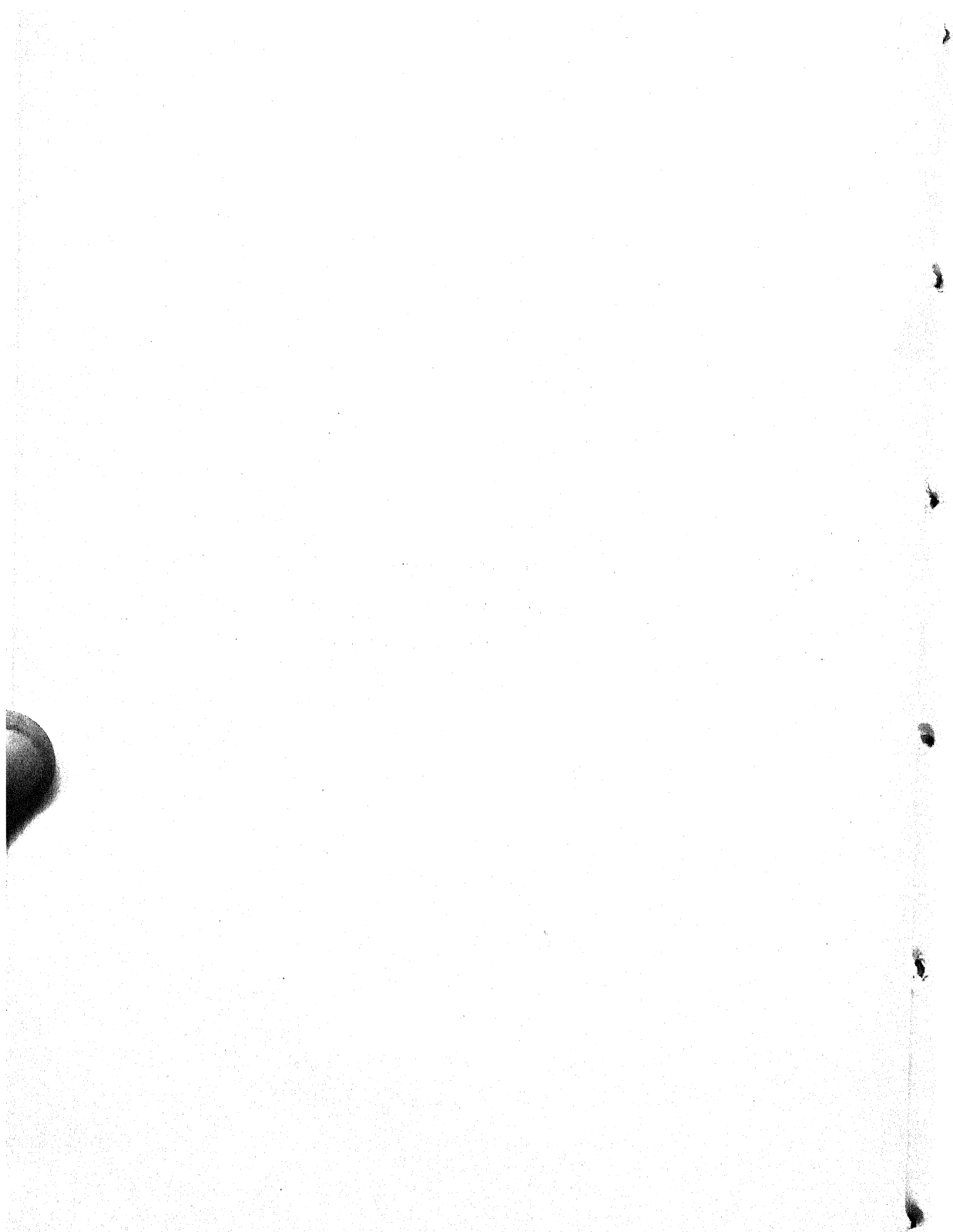
Some of the citrus soils of California, like Hawaiian soils, showed a decreasing water-soluble boron content with increasing depths, but in a relatively few there was an increase with increasing depths and in most there was no definite trend.

Citrus soils in California were found to be generally well supplied with water-soluble boron, and in certain areas the concentrations were excessive.

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THE POTASSIUM-SUPPLYING POWERS OF 20 NEW JERSEY SOILS¹

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It is now recognized that K occurs in the soil in water-soluble, exchange, fixed, and primary-mineral forms. No sharp lines of division occur between these forms, each merging gradually into the one following or preceding it in the list. When fertilizers carrying K are applied to the soil, the element changes from the water-soluble to the exchange form and, if not utilized by plants, it may become fixed by the soil colloids in a nonexchange state. For any given soil type, the extent to which fixation occurs depends upon the K level of the exchange complex, the higher this level, the greater being the fixation.³

The main soil source of K for replacing that removed from the exchange complex by plant roots and drainage waters is the primary minerals. The amount of K in this reserve form is so large in comparison with that in the other three forms that the possibility of its release has long excited the curiosity of soil chemists. The rate at which it will become available to plants might be expected to be somewhat in proportion to its quantity, but such generalizations have not been found to be dependable in agricultural practice.

In connection with a detailed study that is now being made, on a profile basis, of 20 of the most important New Jersey soils,⁴ it seemed desirable to give further consideration to the rate of liberation of the K that is contained in these soils in primary-mineral and fixed forms. Instead of depending upon chemical methods of extraction, however, it was decided to subject representative samples of these soils to the continuous action of plant roots, analyzing both the tops and the roots for their K content. It was recognized, of course, that plant species differ in their capacity to extract nutrient elements from the soil. It was also appreciated that moving a soil from the field to the greenhouse materially alters the conditions within it. But it was thought that it should be possible to obtain values that would be of use in arriving at a decision concerning the relative K requirements of these soils.

OUTLINE OF EXPERIMENT

Large samples of the A horizons of the 20 soils were obtained from typical areas and prepared, by passage through a 4-mesh screen, for greenhouse use.

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² The authors wish to thank S. D. Gray, Northeast Manager of the American Potash Institute, for many helpful suggestions during the course of this study, and the Institute for partly financing the project.

³ DeTurk, E. E., Wood, L. K., and Bray, R. H. 1943 Potash fixation in corn belt soils. *Soil Sci.*, 55: 1-12.

⁴ The locations from which these soils were taken have been recorded, and the records are available in the department of soils.

Two-gallon pots, with solid bottoms, were used as containers, 18 pounds of field-moist soil being placed in each pot. Each soil was adjusted to its calculated optimum moisture content⁵, and was then allowed to stand for several days to attain uniformity of distribution of the water. At the end of that period, the soils were tested by feeling between the thumb and forefinger, and adjustments were then made in the moisture supply of those that did not seem to be at their optimum. The actual dry weight of soil (105° C.) was determined for each pot.

The lime-requirement to pH 7.0 was calculated for each soil, and 100-mesh dolomitic limestone was added as needed to adjust the soils to that value. The limestone and the supplemental fertilizer materials were thoroughly mixed with each lot of soil before it was placed in its pot and before any water was applied. Borax was added at the rates of 5, 10, and 20 pounds per acre⁶ to the sand, sandy loam, and the remaining soils, respectively. These rates of application were in conformity with evidence obtained in other studies dealing with Ca-B relationships in these soils.⁷

Of the ordinary fertilizer materials, only superphosphate and muriate of potash were used. A standard application of 4 gm. 20 per cent superphosphate, equivalent to approximately 200 pounds available P_2O_5 per acre, was made to the soil in each pot. The experimental variable was K, which was added at rates of 0, 340, and 680 mgm. K per pot⁸. The K treatments were approximately equivalent to 100 and 200 pounds K_2O , respectively, per acre.

Alfalfa was chosen as the experimental crop because it is a vigorous-growing perennial that thrives under greenhouse conditions and collects its own N. Thirty seeds of the Hardistan variety were planted in each pot on August 10, 1942. The plants were thinned to ten per pot on September 8, and to four uniform plants on September 28.

At regular intervals throughout the experiment, the original weight of each pot of moist soil was restored by the addition of water. These intervals were weekly in the summer and biweekly in the winter. A uniform quantity of water was added to all pots between these intervals, whenever the condition of the soils or plants seemed to indicate the need for it. At each regular watering the pots were rotated on the benches in such a manner as to have all of them subjected to as nearly identical light and other conditions as possible.

The first crop was harvested December 22, 1942, and six other crops on February 26, April 6, May 11, June 10, July 15, and August 23, 1943. An eighth crop was harvested October 15 from the pots of Collington, Dutchess, and Penn soils, but the data on these extra crops are not included in this article. At the end of the experiment the roots were screened from the soil, washed, dried, and weighed.

Each treatment was triplicated. Since there were 20 soils and three rates of

⁵ Fifty per cent of its moisture-holding capacity by the Hilgard method.

⁶ The term "acre" as used in this article refers to 2 million pounds of air-dry soil.

⁷ Reeve, E., Prince, A. L., and Bear, F. E. 1944 The boron needs of New Jersey soils. N. J. Agr. Exp. Sta. Bul. 709.

⁸ These three rate-of-K series of pots are known as the No-K, 1-K, and 2-K series, respectively.

K applications for each soil, 180 pots were involved. The produce of each pot was oven-dried and weighed separately, but the triplicates were combined before being milled for analysis. Similarly the soil of the triplicate pots was combined and mixed before being sampled for final laboratory examination. The chemical analyses in this report, therefore, are for combined triplicate samples, whether of soils or crops.

The soils were analyzed for total K, exchange capacity, exchange-cation content, and pH values, both at the beginning of the experiment and at its conclusion. Determinations were made of the amounts of K in each crop and of the Ca and Mg content of composited samples⁹ of the seven crops. Certain other analyses were also made on these composites, but with them this article is not concerned.

RESULTS AND THEIR INTERPRETATION

The analytical data for the 20 soils as they came from the field, and before they were treated with the liming and fertilizing materials, are shown in table 1. Also included in this table are the pH values of the soils and their content of exchange K at the end of the experiment. It will be noted that the total K in the original soils varied between 1.8 and 109 m.e. per 100 gm. soil. These quantities are equivalent to 0.07 and 4.26 per cent K, respectively. Assuming that the limiting factor in the series receiving no fertilizer K was a lack of this element, as it was designed to be¹⁰, the highest-yielding soil on the basis of its content of total K should have been the Hagerstown loam. Examination of table 2, however, in which the soils are arranged in accordance with their crop-producing powers without the use of KCl, reveals that the Hagerstown soil ranks 15th in the list. No correlation whatever was found to exist between the total-K content of these soils and their yielding capacity, although the Lakewood sand, the soil that was lowest in total K, was the least productive.

The amount of K in the exchange form was a more reliable index to the K-supplying power of the soil, the highest yields (table 2) having been produced on the Dutchess, Collington, and Penn soils, containing 0.70, 0.48, and 0.40 m.e. exchange K, respectively, per 100 gm. soil, and three of the lowest four yields, on the Sassafras loamy sand, Sassafras sand, and Lakewood sand, containing 0.055, 0.001, and 0.006 m.e. exchange K, respectively.

When KCl was added at the rate of 200 pounds K_2O per acre, the percentage increase in yield was least for the Dutchess, Collington, and Penn soils, and most for Sassafras sand and the Papakating and Lakewood soils. In general, the lower the yield of the soil under conditions in which a deficiency of K was the experimentally designed limiting factor, the greater was the percentage increase in yield of the alfalfa plants following applications of KCl.

⁹ In compositing the samples, the quantities added from each harvest were proportioned to the average yield for that harvest, treatment by treatment and soil by soil.

¹⁰ Plant-tissue tests during the course of the experiment showed no deficiency of P. Dolomitic limestone was used. Chemical evidence as to the adequacy of the other essential elements is lacking.

Previous studies¹¹ had shown that an abrupt drop in yield of alfalfa tends to occur when the K content of the oven-dry top growth of the previous crop falls below 1 per cent, when its Ca content rises above 2 per cent, or when its Ca-K ratio exceeds 4:1. Using the first of these criteria, it was found that a lack of K was a critically limiting factor on the Gloucester, Hagerstown, and Whippany soils to which no K had been applied (table 3), beginning with the first crop, but

TABLE 1

pH values, exchange capacity, exchange cations, and total K of original soils† and pH values and exchange K of soils at end of experiment*

SOIL TYPE	pH VALUES		EX- CHANGE CAPAC- ITY ORIG- INAL	ORIGINAL EXCHANGE CATIONS				TOTAL K ORIG- INAL	EX- CHANGE K END†
	Orig- inal	End†		H	Ca	Mg	K		
			m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
Dutchess shale loam.	7.2	6.7	14.8	0.0	15.3	3.5	0.700	36.1	0.125
Collington loam.	4.7	6.4	15.9	9.2	4.5	1.3	0.482	35.1	0.181
Penn silt loam.	4.5	5.9	19.8	15.3	0.4	1.6	0.407	66.3	0.315
Washington loam.	4.6	6.2	11.3	7.4	1.6	1.9	0.169	53.7	0.086
Hoosic loam.	6.9	7.0	11.4	1.3	8.1	1.0	0.141	65.2	0.118
Sassafras loam.	4.5	6.0	7.5	7.0	0.4	0.4	0.231	32.1	0.095
Dover loam.	7.3	7.0	14.0	0.0	9.6	3.5	0.222	57.9	0.146
Bermudian silt loam.	6.1	6.0	13.2	2.9	6.4	3.4	0.180	57.2	0.171
Colts Neck sandy loam.	4.2	6.8	9.9	7.1	0.2	0.3	0.127	17.9	0.081
Lansdale silt loam.	4.6	6.5	13.0	7.5	3.3	1.5	0.359	38.3	0.174
Chester loam.	5.8	6.9	10.6	5.6	1.5	1.1	0.174	76.7	0.199
Merrimac silt loam.	4.4	6.9	10.2	8.1	0.03	1.5	0.133	36.4	0.078
Fox gravelly loam.	7.4	7.6	8.5*	0.0	6.1	3.1	0.175	64.9	0.085
Gloucester loam.	5.4	6.1	11.9	5.6	1.7	0.6	0.115	57.9	0.063
Hagerstown loam.	7.7	7.7	16.5*	0.0	12.9	4.2	0.219	108.7	0.188
Whippany silt-clay loam.	5.2	6.2	8.7	4.4	3.2	1.5	0.144	42.5	0.063
Sassafras loamy sand.	4.4	6.5	2.7	3.0	0.01	0.00	0.055	32.5	0.120
Sassafras sand.	3.9	5.5	2.0	1.9	0.01	0.00	0.001	8.9	0.000
Papakating stony loam.	5.6	6.6	9.0	3.8	4.0	0.7	0.331	44.3	0.146
Lakewood sand.	4.4	5.2	2.8	2.4	0.07	0.07	0.006	1.8	0.018

* Exchange values are expressed as m.e. per 100 gm. soil. In those cases in which the exchange capacity is greater than the sum of the quantities of the exchange cations, the soils contained free carbonates. One milliequivalent K is equivalent to 0.0391 per cent, or 782 pounds K per 2 million pounds soil.

† With the exception of the Dutchess, Fox, Hagerstown, and Hoosic, these soils came from areas that were believed never to have been farmed.

‡ These analyses were made on the soil of the 2-K series of pots.

that it had not become critical on the Penn, Lansdale, and Chester soils at the time of harvesting the seventh crop.

Ca determinations were made on the seven-crop composites from all three series of pots. These revealed (table 3) that the Ca content of the produce of the

¹¹ Hunter, A. S., Toth, S. J., and Bear, F. E. 1943. Calcium-potassium ratios for alfalfa. *Soil Sci.*, 55: 61-72.

No-K series of pots exceeded the critical 2 per cent on the Fox, Hagerstown, and Papakating soils, and that the Ca-K equivalent ratio exceeded the critical 4:1 on these three, and on the Hoosic, Gloucester, Whippany, and Sassafra (sand) soils in addition.¹²

In order to estimate the rate at which the reserve K of these soils moved into the exchange form, calculations were made, the data from which are presented in table 4. The columns headed "Released by soil" show both positive and

TABLE 2

Total yield and K content of tops and roots of seven crops of alfalfa grown on 20 New Jersey soils with and without added K

SOIL SERIES*	WEIGHT OF TOPS			K IN TOPS		WEIGHT OF ROOTS		K IN ROOTS	
	No K	2 K†	Increase 2 K over No K	No K	2 K	No K	2 K	No K	2 K
	gm.	gm.	per cent	per cent	per cent	gm.	gm.	per cent	per cent
Dutchess.....	68.5	66.5	-3	1.35	1.78	22.7	30.4	0.24	0.45
Collington.....	58.2	63.9	10	1.95	2.41	15.7	14.2	0.37	0.54
Penn.....	56.8	46.6	-18	1.40	2.01	24.8	18.7	0.61	0.80
Washington.....	54.3	60.6	12	1.16	1.75	12.2	18.4	0.20	0.24
Hoosic.....	51.8	62.5	21	0.92	1.55	10.8	15.7	0.23	0.38
Sassafra.....	49.3	62.3	26	0.95	1.53	13.2	17.8	0.34	0.32
Dover.....	45.1	50.2	11	0.97	1.59	12.3	20.3	0.20	0.41
Bermudian.....	41.7	48.9	17	1.28	1.69	4.7	8.7	0.34	0.49
Colts Neck.....	41.5	53.0	28	1.02	1.54	9.7	18.3	0.25	0.22
Lansdale.....	40.8	52.8	29	1.23	1.71	5.9	10.2	0.35	0.82
Chester.....	40.3	49.4	23	1.90	2.21	7.0	11.5	0.51	0.80
Merrimac.....	33.4	50.9	52	0.94	1.60	6.7	16.0	0.24	0.39
Fox.....	31.6	38.3	21	0.96	1.77	6.7	8.8	0.45	0.53
Gloucester.....	28.6	47.4	66	0.82	1.61	1.5	12.5	0.33	0.15
Hagerstown.....	26.7	49.6	86	0.76	1.33	2.3	13.3	0.30	0.33
Whippany.....	20.0	36.0	80	0.77	1.50	1.4	6.4	0.16	0.18
Sassafra.....	17.1	28.7	68	0.91	1.95	1.9	9.3	0.31	0.55
Sassafra.....	15.3	33.8	121	0.84	1.76	3.4	14.4	0.21	0.24
Papakating.....	12.7	35.4	179	1.01	1.51	0.8	10.4	0.49	0.51
Lakewood.....	10.8	31.3	190	0.85	1.79	2.2	11.3	0.20	0.35

* All soils are arranged in the same order in all tables. This order was determined by the crop-producing power of the soils without the use of K, when all other factors were at an intended optimum.

† 2 K indicates 680 mgm. K per pot or 200 pounds K₂O per acre, in contrast to 1 K, where half this amount was used, and No K, where none was used.

negative values, indicating both release and fixation. The Chester soil was outstanding in its capacity to continue to supply K, whereas the Papakating showed an extremely high fixation. Similarly the Collington, Penn, and Bermudian soils released large amounts of K, whereas considerable fixation apparently occurred in the Dutchess, Hagerstown, and Whippany soils.

¹² The Ca-K equivalent ratio may have been greater than 4:1 on some of the individual crops harvested from the other 13 soils, even though this was not true of the seven-crop composites.

It will be noted that the amount of K removed with the crop was greatly increased by the 680-mgm. application of K that was made to each pot on the 2-K series (table 4). Over 60 per cent of the added K was recovered in the seven crops. This was more largely accounted for in the increased percentage K in the harvested crop (table 2) than in the increased yield resulting from the use of KCl. Thus the average increase in the amount of K per unit of produce for the 2-K series of pots was a little over 60 per cent, whereas the average yield-increase was slightly less than 30 per cent. The K content of the first three crops was espe-

TABLE 3

Percentage of K in seven successive crops of alfalfa without added K, crop after which lack of K became limiting factor, and Ca content and Ca-K ratio of seven crops

SOIL SERIES	CROP 1	CROP 2	CROP 3	CROP 4	CROP 5	CROP 6	CROP 7	COMPOSITE 7 CROPS*	
								Ca	Ca-K ratio
								<i>per cent</i>	
Dutchess.....	1.75	2.18	1.55	1.25	1.05†	0.93	0.82	1.53	2.2
Collington.....	2.38	3.44	3.21	1.92	1.31	1.26†	0.97	1.08	1.1
Penn.....	1.45	2.02	1.60	1.33	1.04	1.07	1.13†	1.49	2.1
Washington.....	1.59	1.71	1.17†	0.99	0.91	0.74	0.82	1.44	2.4
Hoosic.....	1.33	1.15†	0.96	0.71	0.74	0.76	0.70	1.96	4.2
Sassafras.....	1.46	1.43†	0.99	0.85	0.65	0.67	0.75	1.58	3.2
Dover.....	1.23	1.28†	0.99	0.78	0.73	0.82	0.75	1.84	3.7
Bermudian.....	1.48	1.88	1.45†	0.84	0.78	1.09	1.02	1.64	2.5
Colts Neck.....	1.02	1.45†	0.96	1.00	0.71	0.77	1.07	1.62	3.1
Lansdale.....	1.43	1.42	1.04	1.17	1.02	1.20	1.03†	1.86	3.0
Chester.....	1.98	2.81	2.68	1.74	1.38	1.52	1.28†	1.52	1.6
Merrimac.....	1.34	1.17†	0.92	1.03	0.53	0.53	0.93	1.52	3.2
Fox.....	1.18	1.51	1.12†	0.74	0.82	0.67	0.72	2.08	4.2
Gloucester.....	0.80†	0.88	0.96	0.64	0.73	0.56	0.97	1.70	4.1
Hagerstown.....	0.73†	0.70	0.69	0.70	0.79	0.86	0.96	2.19	5.6
Whippany.....	0.91†	0.97	0.70	0.79	0.54	0.55	0.65	1.76	4.5
Sassafras.....	1.11†	0.99	0.86	0.85	0.76	0.76	0.79	1.71	3.7
Sassafras.....	1.06†	0.73	0.97	0.75	0.71	0.43	0.64	1.88	4.4
Papakating.....	1.18	1.09†	0.92	0.96	0.56	0.76	0.00	2.32	4.5
Lakewood.....	1.13†	0.94	0.83	0.73	0.68	0.69	0.60	1.44	3.3

* Ca-K equivalent ratios in composite of seven crops harvested from No-K series of pots.

† Last successive crop containing at least 1 per cent K, a critical lower limit for the element in alfalfa.

cially high on the 2-K series of pots, reaching four times the critical 1 per cent in one case.

The rate of release of reserve K from the soil was reduced and the degree of fixation increased by applications of KCl. This is shown in the smaller positive and larger negative values for the 2-K series of pots than for the No-K series, as can be seen by comparing the data in the two columns headed "Released by soil" in table 4.

The individual-crop yield records for the 2-K series of pots are shown in table

5. As previously indicated, the seed was sown in September and, as a result, the first growth of the alfalfa was somewhat dwarfed because of the short days at that season of the year. Nevertheless, the weight of alfalfa harvested per crop per unit area of the better soils was not far different from that occurring in the field during the regular growing season. Thus 10 gm. oven-dry produce on these pots was equivalent to approximately 3000 pounds hay per acre¹³, and the total yield of the seven crops of the 2-K series on the Dutchess shaly loam, the highest-

TABLE 4

Original and final amounts of exchange K in soils, K removed by tops and roots of seven crops of alfalfa, and K released or fixed by soil*

SOIL SERIES	NO-K SERIES POTS				2-K SERIES POTS			
	Original in soil	Removed by crops	Final in soil	Released by soil†	Original in soil	Removed by crops	Final in soil	Released by soil†
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
Dutchess‡	1863	1009	407	-447	2543	1385	333	-825
Collington‡	1257	1260	482	485	1937	1694	473	230
Penn‡	1148	994	626	472	1828	1135	889	196
Washington	467	655	122	310	1147	1102	237	192
Hoosic	418	499	385	466	1098	1025	349	276
Sassafras	721	513	225	17	1401	1005	297	-99
Dover	627	473	384	230	1307	893	412	-2
Bermudian	460	548	401	489	1140	867	437	164
Colts Neck	369	447	236	314	1049	857	236	44
Lansdale	967	519	394	-54	1647	987	469	-191
Chester	488	800	484	796§	1168	1183	558	573
Merrimac	385	330	162	107	1065	876	226	37
Fox	512	333	181	2	1192	727	247	-218
Gloucester	329	238	20	-71	1009	781	180	-48
Hagerstown	567	210	259	-98	1247	702	487	-58
Whippany	373	156	13	-204	1053	551	163	-339
Sassafras	157	160	111	114	837	609	344	116
Sassafras	0	137	0	137	680	630	0	-50
Papakating	937	132	261	-544	1617	585	414	-618
Lakewood	19	96	10	87	699	600	57	-42

* Expressed as milligrams per pot of soil, or the produce thereof.

† Plus values mean release; and minus values, fixation.

‡ Eight crops were harvested from these soils.

§ Equivalent to 235 pounds K₂O per acre.

yielding soil, was equivalent to 20,000 pounds hay per acre. That of the Sassafras loamy sand, the lowest-yielding soil, was, however, only 8600 pounds.

The application of 200 pounds K₂O per acre, represented by the 2-K series of pots, delayed for about two crops the drop in the K content of the alfalfa to 1 per cent. Thus the average number of the crop at which this critical percentage K developed was 3 for the No-K series of pots (table 3) and 5 for the 2-K series (table 5). The amount of K removed from the soil of the 2-K series of pots at

¹³ Calculated on a 90 per cent dry-matter basis.

TABLE 5

Yield per pot, seven successive crops of alfalfa on 2-K treatment pots, crop after which lack of K became critical, and K removed to that point

SOIL SERIES	CROP 1	CROP 2	CROP 3	CROP 4	CROP 5	CROP 6	CROP 7	LIMIT* CROP NUMBER	K† REMOVED
	gm.	gm.	gm.	gm.	gm.	gm.	gm.		mgm.
Dutchess.....	7.8	8.5	10.2	10.0	11.5	8.1	10.4	6	1086
Collington.....	7.1	8.3	9.9	10.5	12.5	7.8	7.8	7	1541
Penn.....	7.0	7.0	7.8	7.6	7.5	4.9	4.8	7	935
Washington.....	7.4	7.9	9.4	8.8	11.6	8.5	7.0	5	910
Hoosic.....	7.3	8.9	9.7	9.7	10.8	6.8	9.3	5	820
Sassafras.....	7.3	7.7	9.0	9.3	10.2	9.1	9.7	5	794
Dover.....	6.2	7.9	8.5	7.9	7.6	5.1	7.0	6	752
Bermudian.....	6.5	7.2	7.5	8.6	6.6	6.2	6.3	4	627
Colts Neck.....	5.8	7.7	8.6	8.5	9.0	6.3	7.1	6	754
Lansdale.....	7.7	7.7	10.0	8.0	7.0	6.1	6.3	5	773
Chester.....	5.0	6.1	8.4	8.1	8.9	6.5	6.4	7	1091
Merrimac.....	6.2	6.2	8.2	8.1	8.5	7.2	6.5	4	638
Fox.....	4.2	4.4	5.5	7.2	6.8	4.1	6.1	7	681
Gloucester.....	6.0	7.3	8.9	8.3	8.2	5.0	4.7	4	597
Hagerstown.....	5.6	5.7	7.5	7.9	7.9	7.9	7.1	4	465
Whippany.....	2.8	3.7	4.4	6.2	7.9	6.2	4.8	4	370
Sassafras.....	2.9	4.4	4.5	4.7	4.7	3.1	4.4	7	558
Sassafras.....	3.5	5.2	6.2	6.8	5.5	3.1	3.5	4	498
Papakating.....	4.2	4.6	5.4	5.8	5.3	4.5	5.6	4	387
Lakewood.....	2.9	4.0	5.9	6.5	5.5	3.2	3.3	5	504
Average‡.....	5.7	6.5	7.8	7.9	8.2	6.0	6.4		

* Last of successive crops containing 1 per cent or more K.

† Amount of K removed from soil by alfalfa before a lack of this element became a critical factor in growth of plants.

‡ The averages, at first, indicate the lengthening of the days and, later, the decreasing K content of soils.

TABLE 6

*Grouping of 20 New Jersey soils in relation to K needs**

GREATEST	MARKED	MODERATE	LEAST
Lakewood sand.....	Sassafras loam-sand	Lansdale silt loam	Dutchess shale loam
Whippany si. cl. loam	Hagerstown loam	Sassafras loam	Bermudian silt loam
Sassafras sand.....	Merrimac silt loam	Hoosic loam	Dover loam
Gloucester loam.....	Colts Neck s. loam	Chester loam	Penn silt loam
Papakating stony loam	Fox gravelly loam	Washington loam	Collington loam

* The need of these soils for K fertilizers is in the order shown, the one at the top of each column having the greatest need for K, and the one at the bottom the least.

this point ranged between 370 and 1541 mgm. per pot, equivalent to approximately 110 and 450 pounds K_2O per acre, respectively.

In evaluating the data shown in tables 1 to 5, inclusive, for the purpose of classifying the A horizons of the 20 soils in relation to their need for K in fertilizer form, three criteria were employed. These were the content of exchange K in the soils as they came from the field, the response of the alfalfa when K applications were made to them, and the extent to which their reserve K was released for plant use. Using these criteria, the soils have been arranged into four groups, as shown in table 6.

It is apparent that the rating for any given field of any one of these types of soil might well be higher or lower than is indicated by the classification, depending upon the treatment it has received at the hands of the operator. Thus the position of the Dutchess soil is probably not what it would have been if a virgin sample of that soil had been studied. Records on the field from which that sample was selected show that it had received about 60 tons of manure per acre during the 10 years just previous to the time the soil was chosen for study. This particular location was selected because of other research work in progress on that field.

The same applies to the Fox, Hagerstown, and Hoosic soils, although to a much less extent, since these three soils were chosen from fields that showed less evidence of good management within recent years. The ratings of all 20 soils are tentative, however, and may have to be changed when further evidence has been accumulated.

SUPPLEMENTAL OBSERVATIONS

Although the A horizon materials used in these tests were only the top portions of the profiles of these soils, they represent that portion in which young plants get their start and from which the major part of their mineral-nutrient supply is derived. This is especially true of short-season annual crops, but it applies to a surprisingly large degree to perennials as well.

The average exchange capacity of the A horizons of these 20 soils at the time they came from the field was greater by 1.7 m.e. per 100 gm. soil than it was at the end of the experiment. This suggests rapid oxidation of organic matter as a result of the thorough aeration the soils underwent during their period of preparation for use in the pot tests. The lowering of the exchange capacity was greatest in Penn silt loam.

Some limiting factor or factors operated in those members of the group whose productivity rating placed them at the bottom of the list, otherwise the addition of KCl should have raised the yields of these less productive soils to a point approaching those of the soils at the top of the list. Even with the 2-K treatment, however, the four lowest yielders produced only about one half as much alfalfa as the four highest yielders. A series of other studies are being made to determine what these limiting factors are.

Except for the Collington and Penn soils, the weight of roots was greatly increased by K applications. Under field conditions, this extra K in the roots might well be an important factor in determining the length of life of the alfalfa stand.

The fact that alfalfa tends toward luxury consumption of K, having the capacity to take up several times as much of the element as is required for maximum yields, indicates that repeated use of smaller amounts of KCl during the plant's period of growth may be more effective than one large application at the time of seeding, particularly on the sandier types of soil. It seems probable that the yields of those soils with a low exchange capacity would have been materially increased if the total amount of K applied had been divided into as many applications as there were crops harvested. This is being investigated as one of the possible factors limiting yields on such soils.

Fixed K is not permanently lost to plants, but constitutes a different type of reserve from that in the primary-mineral form, being more readily available to the crop in time of need. It should be kept in mind that this experiment was conducted in the greenhouse, and the benefits from winter resting of the soils were not realized. Thus, under field conditions, a good bit of the fixed K would probably have been released for use by the first crop of each new season.

Under practical farming conditions, the amount of K stored in the exchange complex is determined not alone by the inherent nature of the soil, but by the farmer's soil-management program. Nevertheless, the relative ratings of most of these soils should hold in practice, if identical systems of management were being applied to all of them. Thus a Collington soil can always be expected to have a considerably greater capacity to yield the necessary K to plants than a Sassafra soil of the same class under the same system of management.

SUMMARY AND CONCLUSIONS

This study had for its purpose the evaluation of the A horizons of 20 important New Jersey soils in relation to their capacity to yield their reserve K to the alfalfa plant. The alfalfa was grown through seven successive crops under greenhouse conditions in which the experimentally designed limiting factor, in the first series of pots, was a lack of K.¹⁴ This deficiency was partly or totally eliminated in the second and third series of pots by applications of KCl equivalent to 100 and 200 pounds K₂O, respectively, per acre.

The total and exchange K were determined on the soils as they came from the field and after the seven crops of alfalfa had been harvested. Analyses for K were made of the crops, as harvested, and of the roots, at the end of the test. The Ca and Mg contents of the soil exchange-complex and of the harvested crops were also determined. From the data thus obtained, calculations were made of the amounts of K released by the several soils during the course of the experiment.

The data verified the previously known fact that the most reliable index to the capacity of a soil to supply K to the crop is not its total content of the element but the amount that exists in the exchange form. It was shown, however, that the soils studied vary enormously in their capacity to renew the exchange supplies from their reserves of K. Some soils, of which Chester loam was the best example studied, continued to release large amounts of K throughout the period of

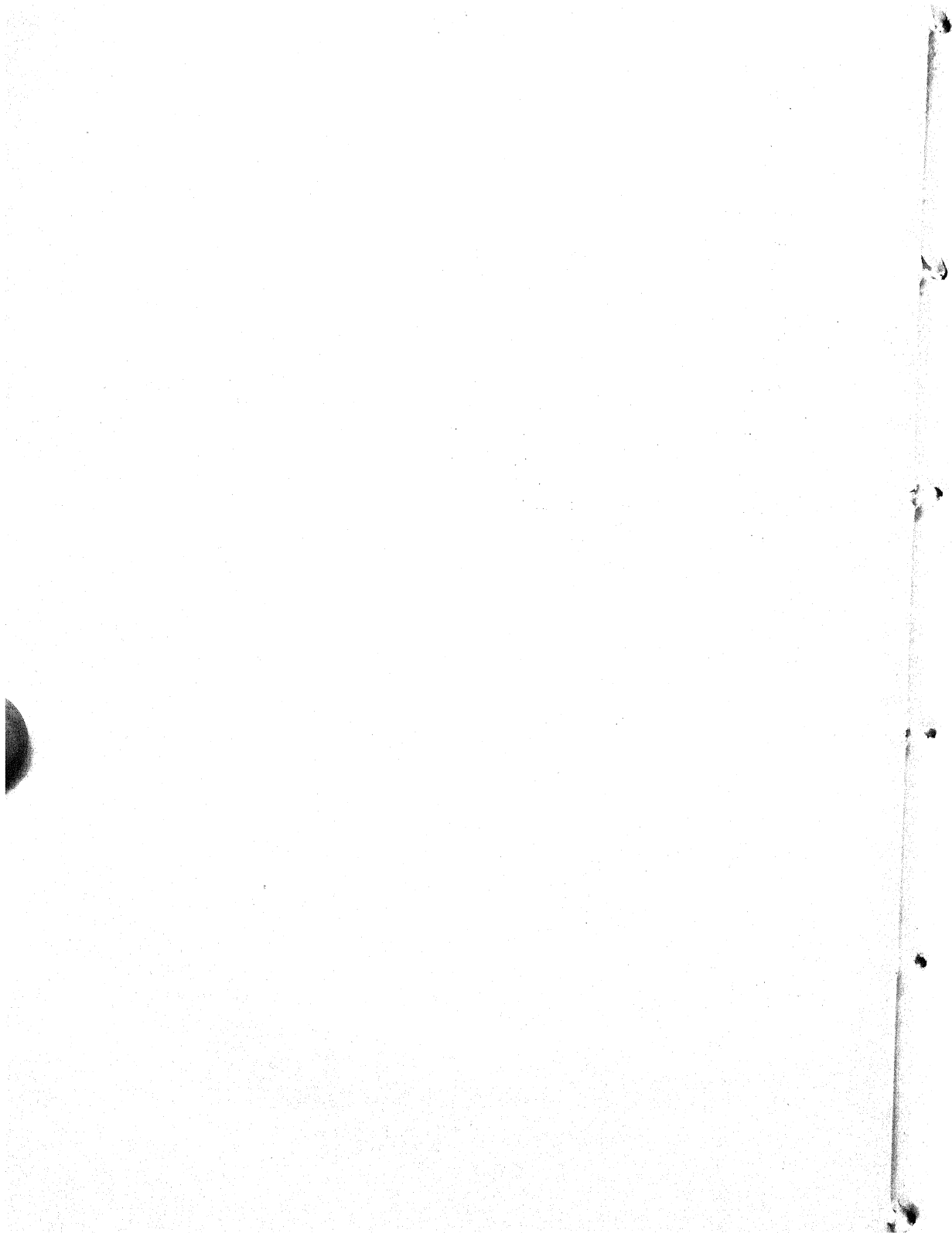
¹⁴ A few of these soils naturally contained adequate amounts of available K, but in most of them a lack of it limited the growth of the alfalfa.

the test. Other soils, of which Papakating stony loam was an outstanding case, were in greater need of fertilizer K than would have been anticipated from a knowledge of either their total or their exchange supplies of the element.

Some factor or factors other than a lack of K limited the growth of alfalfa on 15 of the 20 soils. The yields of the lowest-producing soils could not be raised to 50 per cent of those harvested from the most productive members of the list, when K, the supposedly limiting factor, was supplied in what was believed to be adequate amounts.

In rating the soils according to their K requirement, it was found that Lakewood sand, Whippany silty clay loam, Sassafras sand, Gloucester loam, and Papakating stony loam had the greatest need of K, and Dutchess shale loam, Bermudian silt loam, Dover loam, Penn silt loam, and Collington loam, the least, the other 10 soils occupying intermediate positions.

This is one of a series of studies designed to determine what factors limit crop production on this selected list of soils, to rate these soils with respect to each of these factors, and to ascertain the means by which such limitations can best be overcome. It should be possible to eliminate unfavorable influences, one by one, and to bring the productivity of all of these soils to the same level, that level being determined by external conditions and the inherent capacity of the experimental plants to produce.



PHOSPHATE STUDIES: II. CHEMICAL AVAILABILITY OF PHOSPHORUS IN VARIOUS ORGANIC AND INORGANIC CARRIERS, AS INDICATED BY THE NEUBAUER TEST¹

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CHEMICAL AVAILABILITY

With but few exceptions, whenever the unmodified term "available" has been employed in reference to elements of plant food, the designation has been based upon chemical considerations only. In the interpretation of plant-growth tests or other tests wherein differences in the performance of a nutritive element in carriers of various chemical compositions are observed, it is customary to say that the element is "available" in different degrees, in the different carriers, and to ascribe the variation to known or supposed differences in molecular composition, solubility, nature of ions produced, and, perhaps in some instances, even molecular structure. These characteristics are all of a chemical nature; even solubility, although classed as a physical property, derives from chemical properties, since it depends upon the molecular relations of water to other substances.

There is, however, another type of circumstance, not derived from chemical considerations, which also plays a part in determining the availability of substances to plants. This category embraces effects due to the location of the material with respect to the feeding portion of the root system. Since influences of this kind upon the effectiveness of a substance in plant nutrition depend upon the positional relations between the plant and the substance, Spencer and Stewart, in 1931 (12), proposed the term "positional availability." In the results of numerous experiments on fertilizer placement there is evidence that the positional factor does operate, and in many instances to a degree that is of practical importance. Reports of greenhouse investigations by Gile and Carrero (5, 6), Auchter (2), Spencer (13), and McMurtrey (9) present evidence of a more fundamental nature bearing on the same question.

In anticipation of reporting studies dealing with the positional factor, Spencer and Stewart were confronted with the question of how to designate this factor. If a plant-food element is chemically bound in such a way as to render it suitable

¹ Contribution from the soils department, Nevada Agricultural Experiment Station; published with the permission of the director.

² During the progress of the work herein reported, which was done in 1938, the junior author was employed in this laboratory by the Monsanto Chemical Company, of St. Louis, Missouri, under a research fellowship granted to this department by that company. The authors gratefully acknowledge the financial assistance given by the company, and the helpful cooperation afforded by Carroll A. Hochwalt, of the Thomas and Hochwalt Laboratories, Dayton, Ohio, Research Division of the Monsanto Chemical Company, during this and other work under the fellowship.

for nourishing a plant, but is out of reach of the feeding roots, can it properly be considered unavailable to the plant, or should some other term be used? Along with "unavailable," those authors considered "unreachable" and "inaccessible," but chose "unavailable" as seemingly the most appropriate. One of the denotations of the word "available" given in Webster's New International Dictionary³ is "at disposal; accessible or attainable." It is, therefore, as proper to say that an element may be available or unavailable depending upon its positional relation to the plant, as it is to use the same terms in reference to the chemical nature of the substance carrying the element. But since the unqualified term "available" does not distinguish between the chemical and positional factors, both of which are involved in availability in its complete sense, the more specific expressions "chemically available" and "positionally available" were adopted.

From the foregoing it is clear that the authors mean to express, by "chemical availability," essentially what has long been and is now generally implied by "availability," a term that has now and again been recognized as vague (4, 7, 10). An exhaustive discussion of the meaning of "availability" is not essential to this report; but a few points should be mentioned briefly, to indicate what the authors mean by "chemical availability" and how they employ the term in interpreting the experimental results.

1. The Neubauer test, as used in these experiments, is considered as furnishing an indication of relative chemical availability only, and is not viewed in the light of measuring either the total amount of a chemically available plant-food element in the soil or a fractional amount of more limited definition, such as "quickly available," or the like.

2. It is the plant-food element itself—and not an ion, or any substance containing the element—which is considered as possessing chemical availability.

3. Ordinarily, a soil test deals with a soil as a whole, and not just certain fractional parts of it. Any natural soil, the authors assume, contains a given plant-food element in various chemical forms. There are probably many such forms which are unknown, both as to quantity and chemical make-up. In any event, unless at least one of all the forms present is positively known to have given up none of the element whatever to a plant or an extracting solution, then all the forms must be recognized as possibly having contributed in some degree to the result of the test. Hence it is all of the element in the soil, lumped together and considered in the aggregate, which is referred to in speaking of the chemical availability.

4. Emphasis is placed upon the *range* in chemical availability. A Neubauer phosphorus value, for instance, as a rule has no meaning if considered entirely alone; its significance lies in how it compares with some other value. Among values obtained from a number of untreated soils, for example, any one of them is of interest only in regard to where it falls within the considerable range covered by the group.

5. As is indicated under point 3, it is a soil's total content of a plant-food element, considered collectively as regards the various forms containing it, of which chemical availability is viewed as an attribute. This applies to any untreated soil; and of course, in the last analysis, to any treated soil as well. In the case of treated soils, however, it is always desired to compare different treatments, or one treatment with no treatment. Most soil tests give determined quantities of the element, as the basis for comparison; and if the quantity obtained from the treated soil is greater than that from the untreated, the difference is commonly assumed to be some of the element added in the treatment. On that assump-

³ Second edition, unabridged; G. and C. Merriam Co.; 1935.

tion, it is permissible to speak of the chemical availability of the element in the carrier, as distinguished from that native to the soil, as long as the conclusion about it is limited to the soil used and other conditions of the test. The chemical availability of the element in different carriers will vary, just as in the case of untreated soils; and here, too, the primary concern is not what a given value is, in an absolute sense, but its relative position in the range of values.

OBJECT, AND CERTAIN REQUIREMENTS, OF THE EXPERIMENTS

In a previous report, Spencer and Stewart (12) advanced the hypothesis that the availability of applied phosphorus might be increased by improving the positional relation of the phosphorus to the root system, through use of a soil-penetrating type of organophosphate. The proof or disproof of the validity of that hypothesis must await the results of field experiments in which penetrating and nonpenetrating phosphates are compared. As a rule, only in the field can root systems develop normally in configuration and extent, and therefore field studies provide the only adequate means of evaluating the practical effects of the positional factor in availability. But in any case, no benefit through increased positional availability could be expected unless the phosphorus applied in the penetrating form possessed good chemical availability also, for penetration could avail nothing if that which had penetrated were not then able to nourish the plant adequately.

It is thus desirable to determine the chemical availability of the phosphorus in various soil-penetrating forms which might be employed in the field in attempts to achieve more efficient performance of applied phosphorus through its deeper permeation of the soil mass. That was the object in these experiments. In this work, the chief interest centers not in organophosphates in general, but in those which have appreciable penetrative power. The data presented include results obtained with monoethyl calcium phosphate, and also its acid salt. The monoethyl ester has thus far shown little capacity for soil penetration, but as it is present in appreciable quantity as a coproduct with diethyl calcium phosphate (a good penetrator) in the "crude calcium ethyl phosphate" also reported, the chemical availability of its phosphorus is of interest.

In this project one of the major purposes, toward the achievement of which the determination of chemical availability is only one of the necessary steps, is to determine the effects of positional relations between applied phosphate and plant under natural (field) conditions. Certain of these relations, in the field situation, depend upon movement of the phosphate through the soil. It was therefore essential to make the chemical availability tests under the conditions of soil-phosphate contact, for during such contact chemical changes undoubtedly occur, both to organic and inorganic phosphates, which do not take place when a phosphate is tested in a nutrient solution or in a medium of pure quartz sand. Use of either of the last two mediums might, then, give an erroneous picture of what to expect in the way of chemical availability in the field.

It was also considered that a plant-growth test, rather than any test based on the behavior of chemical reagents, affords the best means of estimating the chemical availability of a nutritive element. As has been shown by Thornton

(14) and others, the Neubauer method is well adapted to a problem of this kind; hence this method was chosen.

EXPERIMENTAL

Equipment for making Neubauer tests

A constant-temperature room⁴ was built in the laboratory, for growing Neubauer cultures. The walls, floor, and ceiling were insulated both with rock wool and with dead-air spaces. The approximate inside dimensions are: length, 12 feet; width, 6 feet; height, 7 feet. The room stands parallel to the south wall of the building, and 6 feet from it. In this building wall are two large windows, close together, which admit strong diffused light, but not direct sunlight, into the constant-temperature room through a long, double-sashed window. For Neubauer cultures, the light thus admitted has proved excellent. The walls and ceiling are painted white.

The room is equipped with a refrigeration unit, heating strips, and a humidistat, so that temperature and humidity are automatically controlled. Near the ceiling, in one corner of the room, a fan operates constantly through the cooling unit and heater strips, against a baffle so placed that the air current is directed against the window, and thus not directly over the cultures, which are accommodated on a bench 33 inches wide running the full length of the room on the side away from the window. Fresh air from out of doors is brought into the room through a 3-inch duct passing through the east walls of both the building and the constant-temperature room; for use in cold weather, this duct contains a heating unit controlled by a thermostat. At another location in the same wall of the room, a small blower evacuates air into the laboratory through a 2-inch duct, and thus draws in the fresh air through the 3-inch duct. The temperature can be held constant to $\pm 1^\circ \text{F}$.

Procedure for Neubauer tests

The procedure in preparing and growing the cultures was that given by Thornton (14), with only minor modifications. Registered Rosen rye seed⁵ was used. The weight per one hundred seeds was kept constant at $3.07 \pm 0.003 \text{ gm}$. Seeds were dusted with New Improved Semesan Jr.⁶ The temperature was maintained at $70^\circ \pm 1^\circ \text{F}$. Water was added to the cultures by weight, daily or as otherwise required.

For phosphorus determination, the plant material was decomposed by wet oxidation with sulfuric and nitric acids, after which the analysis was completed according to the standard A.O.A.C. gravimetric method.

⁴ This room was constructed in the fall of 1937 according to suggestions made to the authors by S. F. Thornton, at that time soil chemist in the Indiana Agricultural Experiment Station, Purdue University. The authors are indebted to Dr. Thornton for his kind assistance.

⁵ Purchased from G. C. and L. G. Hutzler, South Manitou, Michigan.

⁶ Manufactured by the Bayer-Semesan Co., Inc., of Wilmington, Delaware.

Experiment 1

In this experiment, tests were made of the chemical availability of phosphorus in four inorganic and eleven organic phosphates in a single soil. The soil was obtained from an experimental plot area of the Division of Forage Crops and

TABLE 1

Inorganic and organic phosphates used in tests with Christiana soil from Beltsville, Maryland

PHOSPHATE		FORMULA	PHOSPHORUS	
No.*	Name		Theoret- ical	Found
			per cent	per cent
Inorganic phosphates				
1	Treble superphosphate (Anaconda)	20.65
2	Calcium metaphosphate, TVA #443-A	26.93
3	Fused rock phosphate, TVA	12.32
4	Sintered phosphate	16.17
Organic phosphates				
5	Calcium glycol phosphate	$C_2H_5O_5PCa$	17.30	16.96
6	Calcium glucose-3-phosphate	$C_6H_{11}O_5PCa$	10.41	10.14
7	Monoethyl calcium phosphate	$C_2H_5O_4PCa$	18.88	18.43
8	Diethyl calcium phosphate	$C_4H_{20}O_8P_2Ca$	17.91	17.91
9	Triethyl phosphate	$C_6H_{15}O_4P$	17.03	17.18
10	Monoethyl calcium acid phosphate	$C_4H_{12}O_8P_2Ca$	21.35	21.18
11	Mixture (50-50) of monoethyl and diethyl calcium phosphates	18.10
12	Mixture (50-50) of diethyl calcium phosphate and monoethyl calcium acid phosphate	19.50
13	Calcium salt of phosphates of sugars in blackstrap molasses	6.24
14	Crude "calcium ethyl phosphate"	17.70
15	Mixture (50-50) of monomethyl and dimethyl calcium phosphates	18.40

* Phosphates 5 and 6 were prepared in this laboratory, by methods previously reported (8, 12). For phosphate 2, the authors are indebted to W. H. MacIntire, of the Tennessee Agricultural Experiment Station; for phosphate 4, to K. D. Jacob, of the Division of Fertilizer Research, U. S. Department of Agriculture; for phosphate 3, to the Tennessee Valley Authority; and for phosphates 7 to 15 inclusive, to the Monsanto Chemical Company. Phosphate 1 was purchased from the Anaconda Copper Mining Company.

Diseases, Bureau of Plant Industry, U.S. Department of Agriculture at the Beltsville Research Center, Beltsville, Maryland.⁷ It is of the Christiana type; was taken from the surface to a depth of 7 inches; and has a pH of 7.7.

Information about the phosphates used is given in table 1. Number 14, the

⁷ The authors are indebted to Mason A. Hein, of the Division of Forage Crops and Diseases, for supplying this soil.

crude "calcium ethyl phosphate," contained both monoethyl and diethyl calcium phosphates; both are formed during the process which was used in preparing a large batch of the product for field experiments. This product contained about 26 per cent of the diethyl salt.

The phosphates alone were applied to the soil; i.e., nitrogen and potassium were not included in the treatments. In all cases, phosphate was added in an amount which supplied 5.3 mgm. of phosphorus to each Neubauer culture.

TABLE 2

Uptake of phosphorus in Neubauer tests with Christiana soil treated with inorganic and organic phosphates

PHOSPHATE		UPTAKE OF P BY CULTURES PLANTED AFTER VARIOUS PERIODS OF PHOSPHATE-SOIL CONTACT			
No.	Name	0-day	6-day	18-day	30-day
		mgm.	mgm.	mgm.	mgm.
	(No treatment)	10.5	11.1	11.2	11.0
<i>Inorganic phosphates</i>					
1	Treble superphosphate	12.2	13.1	13.2	12.6
2	Calcium metaphosphate, TVA #443-A	11.9	12.9	13.2	12.9
3	Fused rock phosphate, TVA	11.5	13.1	13.2	12.3
4	Sintered phosphate	11.7	13.3	13.2	12.3
<i>Organic phosphates</i>					
5	Calcium glycol phosphate	12.2	13.0	12.8	12.3
6	Calcium glucose-3-phosphate	11.9	12.7	12.4	12.7
7	Monoethyl calcium phosphate	12.1	13.1	12.9	12.3
8	Diethyl calcium phosphate	12.1	13.2	13.2	12.7
9	Triethyl phosphate	11.5	11.8	11.4	10.9
10	Monoethyl calcium acid phosphate	12.8	13.1	13.0	12.9
11	Mixture (50-50) of monoethyl and diethyl calcium phosphates	12.5	13.5	13.0	13.0
12	Mixture (50-50) of diethyl calcium phosphate and monoethyl calcium acid phosphate	12.4	13.6	12.9	13.1
13	Calcium salts of phosphates of sugars in blackstrap molasses	11.2	12.3	12.0	11.7
14	Crude "calcium ethyl phosphate"	12.3	13.1	13.0	12.8
15	Mixture (50-50) of monomethyl and dimethyl calcium phosphates	12.9	13.0	12.7	12.5

The experiment was designed to include a study of the effects of the added phosphorus after various periods of time in contact with the soil. The required amount of a particular phosphate was thoroughly mixed with a batch of the soil sufficient for 16 cultures. (An exception was that the triethyl phosphate, a water-soluble liquid, was added to each culture individually, in water solution, at the time the 16 cultures were made up.) The 16 cultures were then made up, in petri dishes, ready for planting. Four were planted immediately, giving quadruplicate tests for the "0-day" period of phosphate-soil contact. The re-

maining 12 cultures were moistened, and the dishes were tightly covered with waxed paper to minimize drying. From these, quadruplicate cultures were then planted after 6, 18, and 30 days respectively.

The results from this experiment are given in table 2, in which each value is the average of quadruplicate tests.

TABLE 3

Soils used in testing the chemical availability of phosphorus in crude "calcium ethyl phosphate" (Phosphate 16) and treble superphosphate by the Neubauer method

NO.*	NAME	SOURCE, VICINITY OF	pH (GLASS ELEC- TRODE)
1	Woodstown loam (Coastal Plain)	New Brunswick, New Jersey	6.5
2	Christiana	Beltsville, Maryland	7.7
3	Lisbon clay loam	Des Plaines, Illinois	5.2
4	Wooster silt loam	Wooster, Ohio	4.7
5	Las Vegas loam	Las Vegas, Nevada	9.0
6	Cecil sandy clay loam	Pickens, South Carolina	5.7
7	Aiken loam	Davis, California	5.8
8	Yolo fine sandy loam (subsoil)	Paradise, California	7.2

* The authors are indebted to the following individuals for supplying the soils indicated: 1, Howard B. Sprague, of the New Jersey Agricultural Experiment Station; 3, J. P. McCol- lum, of the Illinois station; 4, J. H. Gourley, of the Ohio station; 6, Wm. R. Paden, of the South Carolina station; and 7 and 8, John P. Conrad, of the California station.

TABLE 4

Neubauer phosphorus values from various soils treated with treble superphosphate and crude "calcium ethyl phosphate" respectively

SOIL		NEUBAUER P VALUES		
No.	Name	No treatment	Treble superphos- phate treatment	Crude "Calcium ethyl phosphate" treatment
		mgm.	mgm.	mgm.
1	Woodstown loam (Coastal Plain)	9.8	11.3	11.3
2	Christiana	11.6	13.9	13.6
3	Lisbon clay loam	13.9	16.3	16.5
4	Wooster silt loam	11.2	13.4	12.3
5	Las Vegas loam	13.8	16.5	16.5
6	Cecil sandy clay loam	9.8	10.7	11.3
7	Aiken loam	11.5	13.9	13.9
8	Yolo fine sandy loam (subsoil)	11.3	17.5	17.1

Experiment 2

A second batch of the crude "calcium ethyl phosphate" had been prepared for field use, and the chemical availability of its phosphorus was tested in several soils. This phosphate (No. 16) was essentially the same as phosphate 14 used in experiment 1, and was given the same name, "crude 'calcium ethyl phosphate'." Its phosphorus content was 15.88 per cent. In this experiment, phosphate 16 and the treble superphosphate included for comparison were

used at the same phosphorus supplying rate and with the same procedure as was employed in experiment 1, except that each treatment was run in triplicate instead of quadruplicate.

The soils used are listed in table 3.

Table 4 gives the results of the tests. Each value is the average of three cultures.

DISCUSSION

Statistical treatment of results

The nature of both experiments reported is such as to allow statistical treatment of the results by "Student's" method for the determination of the significance of differences between means; and this method (11) was applied. For example, the average of the values for the 0-, 6-, 18-, and 30-day contact periods, for no treatment (table 2), is 11.0; the corresponding average for the treble superphosphate is 12.8. Pairing of the no-treatment value with the treble superphosphate value, for each contact period, and analyzing by "Student's" method gives a value for t of 17.294, which corresponds to a P value much lower than 0.01. This indicates odds far greater than 99 to 1 that the average increase for the treble superphosphate is significant. In the analyses of the results, a mean difference is considered significant when $P \leq 0.05$.

Results of experiment 1

All four of the inorganic phosphates gave average values significantly higher than those from no treatment. There was no significant difference between any two of these carriers.

Of the eleven organic carriers, ten gave average values significantly higher than those from no treatment. For one of the ten, however, (phosphate 13, the calcium salts of phosphates of sugars in blackstrap molasses), the increase was only 0.85 mgm. P. This is definitely significant ($P < 0.01$), but is only about half the average increase for the other nine.

Though the value for triethyl phosphate was slightly higher than that for no treatment, the difference was not significant. Conrad (3) has reported finding this phosphate toxic to milo. It appears that the more concentrated solutions of triethyl phosphate he employed added from 60 to 600 per cent more of this compound, per unit weight of soil, than was applied in the present tests. In these latter, there was no evidence of toxicity to the rye plants. A physical property of triethyl phosphate, its appreciable volatility, is of interest, however, in this connection. It was found in this laboratory that percolates and other solutions containing this compound, taken for phosphorus analysis, must be made acid and refluxed thoroughly before evaporation, otherwise much of the phosphorus is lost. (Refluxing for 24 hours in 3 N HCl proved most effective and convenient.) Loss of the compound itself, by evaporation, is shown by the following test: A 50-cc. beaker containing a few grams of triethyl phosphate was weighed, then allowed to stand at room temperature, uncovered, for 50 days, during which time it lost 2.71 gm., or an average of 0.054 gm. (=9.3 mgm. P) daily. It is thus quite probable that some of this compound is lost from the soil in a Neubauer or pot culture, and this loss could affect the result.

Nine of the eleven organic phosphates gave average values not significantly different from one another and not significantly different from any one of the inorganic phosphates.

The average uptake of phosphorus for all the inorganic forms during the four contact periods, is 12.7 mgm. per culture. For all eleven organic forms, the corresponding average is 12.6 mgm., but if phosphates 9 and 13 are excluded (they are obviously in a lower bracket), the average is 12.8 mgm. This is identical with the individual average for treble superphosphate, the highest among the inorganic forms.

The data in table 2 reveal an interesting behavior of the phosphates for the four contact periods. This is brought out in figure 1, in which the curves represent the average performances of (a) the four inorganic phosphates, (b) the nine highest organic phosphates, and (c) no treatment, respectively; for the four periods.

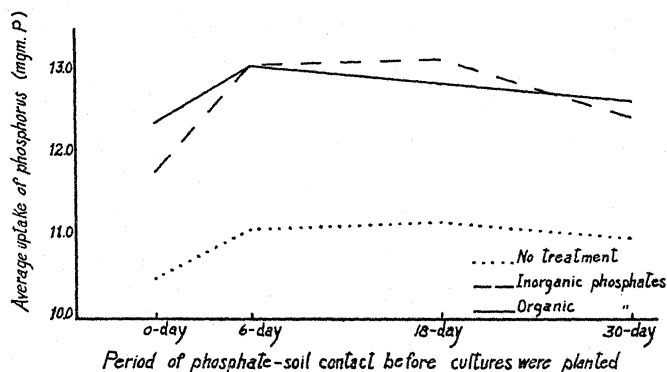


FIG. 1. EFFECT OF VARIOUS PERIODS OF PHOSPHATE-SOIL CONTACT ON CHEMICAL AVAILABILITY OF PHOSPHORUS IN ORGANIC AND INORGANIC CARRIERS, WHEN ADDED TO CHRISTIANA SOIL, IN NEUBAUER TESTS

Perhaps the most noticeable feature of the behavior portrayed in figure 1 is the rather abrupt rise in phosphorus uptake shown by the tests for the 6-day over the 0-day period. Were this true only in the cases of phosphorus addition to the soil, it might appear to be due solely to chemical reactions between the added phosphates and the soil constituents. A similar rise, though not quite so great, is shown, however, by the no-treatment values. Why this is, the authors do not know. The conditions of temperature, moisture content, and other environmental factors, were the same for all the soil portions during the interval between the 0-day and 6-day plantings. Possibly these conditions were such as to improve the chemical availability of the native soil phosphorus, as well as that of the added phosphorus, during that interval. Another factor may have been responsible for, or may have contributed to, the abrupt rise; and that is the matter of light during the growth of the Neubauer cultures. Different average light conditions may have prevailed during the growth periods of the two sets of tests.

For testing the significance of the difference between an inorganic and an

organic phosphate average (such as those graphed in figure 1), "Student's" method is not applicable; hence these differences, for the various contact periods, were tested for significance by another method given by Paterson (11, p. 18). The results show that in the Neubauer tests made immediately after the phosphate and the soil were mixed, the organic phosphate values were significantly higher ($P < 0.01$); after 6 days there was no difference; after 18 days the inorganic phosphate values were significantly higher ($P < 0.01$); and after 30 days there was no significant difference.

After 30 days, the chemical availability of the phosphorus in both types of phosphate had fallen somewhat below what it was on the sixth day, but in each case it was still significantly higher than it was at the start.

It is obvious from this experiment that in the Christiana soil the chemical availability of phosphorus in nearly all the organic carriers used was quite as good as that of this element in the old standby, superphosphate, as well as in some of the newer inorganic forms.

Results of experiment 2

The soils used in experiment 2 cover a wide range in pH and other characteristics. The results (table 4) do not appear to show any consistent relationship between the pH of the soil and the uptake of phosphorus from it when treated with either of the phosphates.

Both the organic and the inorganic phosphate induced highly significant increases in phosphorus uptake over no treatment, but the difference between the effects of the two phosphorus forms is insignificant ($P > 0.4$).

Several of the organic carriers used in experiment 1 have very good penetrative power in the soils used in experiment 2.⁸ As the crude "calcium ethyl phosphate" used in this latter experiment is well representative of these other organic carriers, from the chemical standpoint, it seems probable that their phosphorus would show as good chemical availability in this group of soils.

The results from experiments 1 and 2 show the chemical availability of phosphorus in several organic forms to be on a par with that in inorganic forms. In this respect the results are of the same character as findings reported by Allison, Pinck, and Sherman (1). With a few exceptions, those investigators used different phosphates and soils from those employed in the present study; but they, too, found that phosphorus in several organic forms is as readily used by plants as is inorganic phosphorus. Their data, calculated to the form shown in table 2, reveal that the average of all their Neubauer phosphorus values from six inorganic phosphates (where 4.3 mgm. P was added per culture), in the quartz sand and soils used, is 14.0 mgm. P, and the corresponding average for the ten organic phosphates is 14.2 mgm. P.

Comparison of the present results with those of Allison, Pinck, and Sherman is of interest from another standpoint. Those workers supplied nitrogen and potassium to all cultures—a practice often considered essential, or at least desirable. In the present study, for certain reasons, this was not done; yet the increases in

⁸ Unpublished results.

phosphorus uptake, over no treatment, were essentially the same as were found by Allison, Pinck, and Sherman. As there was no particular phosphate-soil combination common to both investigations, specific comparisons are impossible. Both studies, however, covered a range of soils and of phosphates, and the relative behavior of the rye plants, with and without the addition of nitrogen and potassium, is of interest. With these other elements supplied (1), the increase in phosphorus uptake, over no treatment, averaged 1.7 mgm. for all the inorganic phosphorus treatments, and 1.9 mgm. for the organic treatments. In comparison, the results in the present study (no N or K added) for all inorganic phosphates averaged 1.8 mgm., and for all organics, 1.4 mgm.

SUMMARY

Why "chemical availability" is adopted as a substitute term for "availability," and the authors' interpretation of its meaning and use, are discussed briefly.

Neubauer tests of one soil treated with four organic and eleven inorganic phosphates, and of several soils each treated with one inorganic and one organic phosphate, show that the chemical availability of the phosphorus in nine of the eleven organic carriers is just as high as that in any of the inorganic carriers.

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PHYSICAL CHARACTERISTICS OF SOILS: IX. RELATION BETWEEN ULTRACLAY AND VOLUME OF FLOC

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The flocculation of soil colloids has been studied by several workers from time to time. Russel (12) and Weigner (13) have tried to bring the flocculation of soil colloids in line with the coagulation and flocculation of soils in general.

Puri (5) directed attention toward the influence of the nature of exchangeable bases present in a soil on the flocculation values for different ions and showed that the higher the valency of the exchangeable base, the smaller the flocculation value for a given electrolyte. Almost at the same time, Anderson (1) and Mattson (2) independently came to a similar conclusion regarding the influence of exchangeable ions.

Müller (3), on a purely theoretical basis, calculated that the smaller the radius of the particle, the higher must be the concentration of a given electrolyte to reduce its electrokinetic potential by a given amount. In other words, the smaller the size of particles in suspension, the greater will be the concentration of the electrolyte required for coagulating the suspension.

It will be seen, however, that one particular aspect of the problem has not been studied so far. No attention seems to have been paid to the *volume* of the flocculated mass after it has completely settled. Soil is a polydisperse system. It consists of particles of all sizes. Even the conventional clay fraction (<0.002 mm.) is not homogeneous but consists of particles of various sizes, starting from 0.002 mm. and ending at a much finer size in the truly colloidal region. The contributions of the particles of the various sizes to the volume of the floc must vary with the size. The smaller particles in suspension, which contribute largely to the total surface presented by the dispersed phase, would probably also contribute largely to the volume of the floc.

In the present paper attention is directed toward this problem in particular. The volume of the flocculated mass of clay suspensions, the contribution made toward this value by the particles of various sizes usually present in soils, and the variations produced by altering such factors as pH value, concentration, and time of aging are studied in detail.

DEVELOPMENT OF THE TECHNIQUE

In order to standardize the technique of determining floc volume of soils, preliminary studies were made of the effect of various factors, such as concentration of clay suspension used, nature and concentration of flocculants employed, and time and speed of centrifuging required to produce a compact mass of the flocs.

Clay (<0.002 mm.) was separated from 1 per cent soil suspensions dispersed by the HCl-NaOH method. For determining the floc volume, 4 cc. of the clay

suspension was always used. The chlorides of Ca, Ba, and Al were found to be about equally effective as flocculants, and 1 cc. of 0.25 *N* solution was found to be enough even in the case of highly clayey suspensions. The chlorides of alkali metals, as expected, did not cause flocculation unless much higher concentrations were employed, and even then the effect was rather slow. The centrifugal machine used consisted of an ordinary ceiling fan having necessary attachments for holding three centrifugal tubes at a time and could be worked at the rate of 620 revolutions per minute. The time of centrifuging was found to affect the values considerably at first, but after about half an hour no further decrease in volume took place, as maximum compaction and settling of flocs had occurred by then. The procedure adopted for determining the floc volumes of soils was, therefore, as follows: A 1 per cent suspension was prepared, after maximum dispersion by the HCl-NaOH method, and clay was pipetted off in the usual way. Four cubic centimeters of the clay were put in the measuring tube, 1 cc. of 0.25 *N* CaCl₂ solution was added, and the suspension was centrifuged for half an hour. The volume of the settled mass was read directly from the measuring tube, which was calibrated accurately up to 0.01 cc.

TABLE 1
Mechanical analysis of soils P. C. 13 A. T. and P. C. 245 A. T.

SOIL NUMBER	SUMMATION PERCENTAGE UP TO DIAMETER										
	0.00004 mm.	0.000063 mm.	0.0001 mm.	0.00025 mm.	0.0006 mm.	0.001 mm.	0.002 mm.	0.005 mm.	0.01 mm.	0.02 mm.	0.06 mm.
P. C. 13 A. T.....	27.2	30.7	41.0	49.2	54.5	57.7	62.8	75.7	78.2	82.9	89.5
P. C. 245 A. T.....	9.8	10.2	12.6	20.5	28.6	30.1	46.0	61.2	74.1	84.4	93.7

The reliability of the values obtained by following the procedure outlined was tested on 12 soils by taking each soil in three separate lots and determining the volume of the floc in each case. The values obtained in all cases were almost identical.

EFFECT OF pH ON FLOC VOLUME

Two soils, P. C. 13 and P. C. 245, both acid-treated and free from exchangeable bases, were studied to determine the effect of the pH value on the floc volume. Mechanical and ultramechanical analyses of these soils were determined by the chainohydrometer (9) and the micropipette (10) methods respectively. The results are given in table 1.

To 5-gm. portions of the acid-treated soils varying quantities of NaOH were added and the suspensions allowed to stand 24 hours, after which their pH values were determined. The suspensions thus obtained at different pH values were diluted to give a 1 per cent concentration, and their floc volumes were determined. The clay content was also determined in each case. The results are plotted in figures 1 and 2. Both the floc volume and the clay content increase with the pH value, but whereas the clay content reaches its maximum

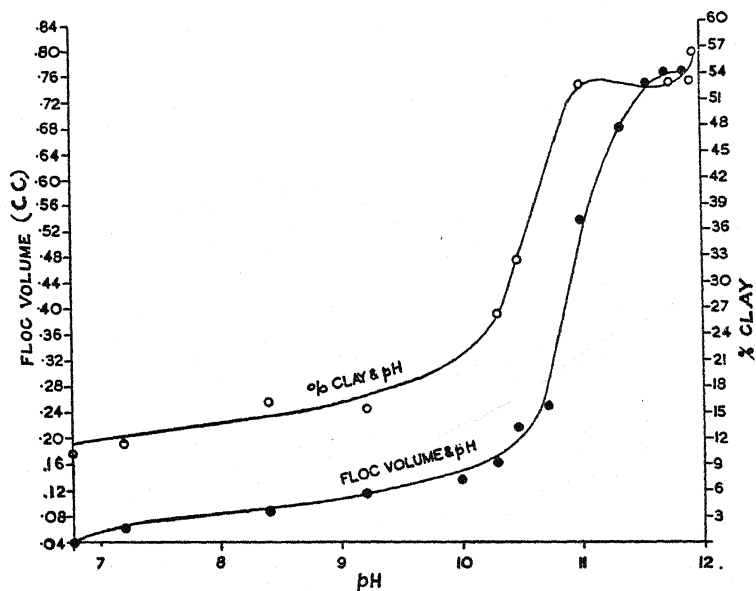


FIG. 1. EFFECT OF pH VALUE ON CLAY CONTENT AND FLOC VOLUME OF SOIL P. C. 13, ACID-TREATED

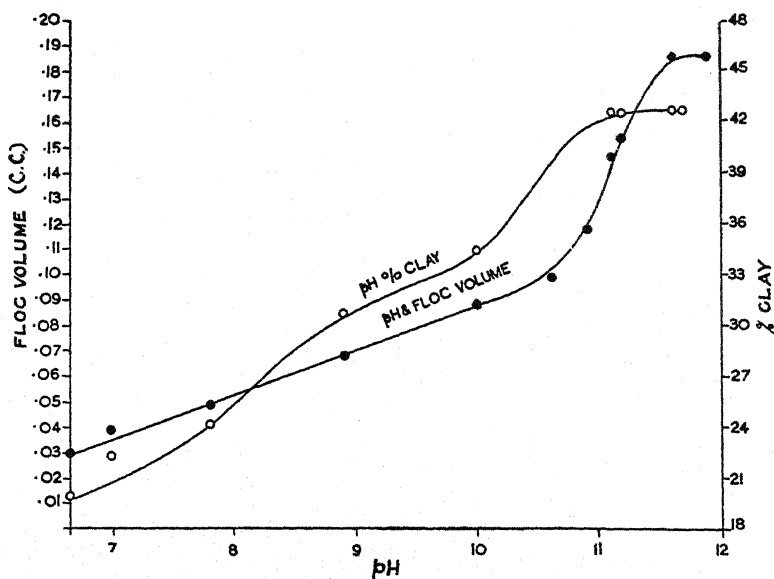


FIG. 2. EFFECT OF pH VALUE ON CLAY CONTENT AND FLOC VOLUME OF SOIL P. C. 245, ACID-TREATED

value at about pH 10.8 the floc at this point attains only a fraction of its maximum value. In fact, the pH-floc-volume curve becomes very steep at this pH and the increase in floc volume is continued to pH 11.6, after which it becomes constant.

Puri and Lal (7) have shown that maximum dispersion in soils, as reckoned on the basis of conventional clay (<0.002 mm.), takes place at pH 10.8. The abrupt increase in the floc volume beyond this pH and its continued increase thereafter show that beyond this point further dispersion takes place. But as the clay content remains virtually constant at pH values higher than 10.8, it appears that it is the clay that is further subdivided into ultraclay particles at these high pH values. This second dispersion—that of clay into ultraclay—is

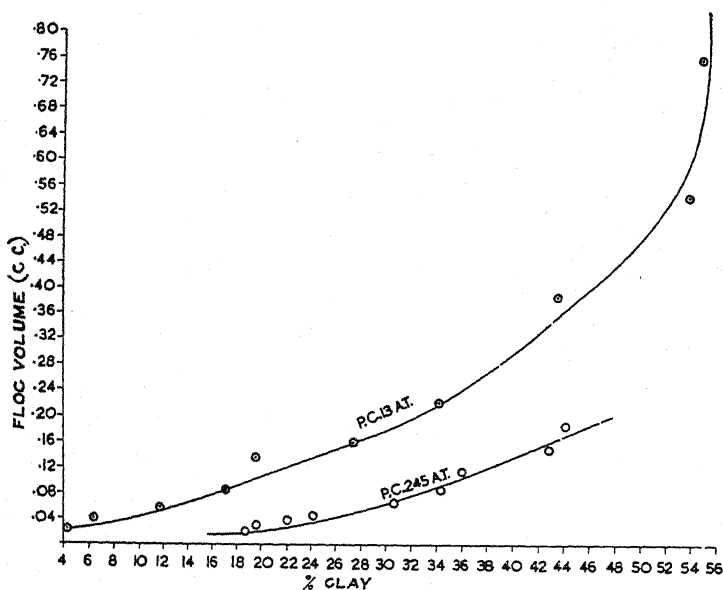


FIG. 3. RELATION BETWEEN CLAY PERCENTAGE AND FLOC VOLUME OF SOILS

completed at about pH 11.6, as beyond this value no increase in floc volume is noticed. It is only at this stage that soil is completely dispersed into its ultimate primary units. Further evidence on this point is offered in the succeeding part of this paper.

The relation between floc volume and clay content is plotted in figure 3. For the same clay content, P. C. 13 soil gives a greater floc volume than does P. C. 245. The reason for this lies in the fact that P. C. 13 is much richer in ultraclay than P. C. 245 (table 1) and therefore a given amount of clay in P. C. 13 contains a larger number of finer particles than does the same amount of clay in the other soil. This obviously leads to the conclusion that size distribution in the ultraclay region, rather than the clay itself, is mainly responsible in determining the floc volume.

For further evidence on this point, another set of experiments was undertaken. It has been shown (8) that a soil dispersed by different methods, though giving almost equal values for clay content, gives entirely different values for various sizes of ultraclay. For instance, the methods involving acid treatment yield much higher values for ultraclay than the other methods. In order, therefore, to decide conclusively whether it is conventional clay (<0.002 mm.) as a whole or the so-called ultraclay particles which are primarily responsible for the floc volume, three soils were dispersed by the HCl-NaOH method (4), the Na_2CO_3 -NaOH method (6), and the sand method—in which the soil is shaken 24 hours with five times its weight of 1-mm. sand particles—a mechanical method of dispersion which has been shown to give maximum clay content (11). The values for clay (<0.002 mm.), ultraclay (<0.0001 mm.), and the flocculated volumes are given in table 2.

Although clay content is almost the same in every soil, irrespective of the method of dispersion, floc volume is different and so is ultraclay. As ultraclay

TABLE 2
Floc volume of soils when dispersed by different methods

SOIL NUMBER	CLAY BY DIFFERENT METHODS			PARTICLES <0.0001 MM. BY DIFFERENT METHODS			FLOC VOLUME BY DIFFERENT METHODS		
	Sand method	Na_2CO_3 method	HCl-NaOH method	Sand method	Na_2CO_3 method	HCl-NaOH method	Sand method	Na_2CO_3 method	HCl-NaOH method
	per cent	per cent	per cent	per cent	per cent	per cent	cc.	cc.	cc.
P. C. 13 A. T.....	53.9	55.0	57.5	3.1	8.1	35.3	0.06	0.16	0.42
P. C. 123 A. T.....	72.1	76.0	77.5	2.0	7.2	11.2	0.02	0.12	0.22
P. C. 245 A. T.....	37.8	39.0	42.7	1.3	5.7	6.2	0.01	0.10	0.11

increases when the soil is dispersed by the acid treatment, so does the floc volume. The discrepancy in the values of floc volume for the same values of clay content is so great that it is absolutely useless to attempt any correlation between conventional clay and floc volume. The correlation, if any, must be looked for in the percentages of particles of various sizes in the ultraclay region. It is not unlikely that the correlation will not depend on particles of any particular size but will rest with the whole size distribution in the region of ultraclay.

In this connection, table 2 shows also that although P. C. 123 contains much more clay than P. C. 13, it gives a lower value for the floc volume. This is because P. C. 13 is richer in the ultraclay fractions.

EFFECT OF AGING

During the course of these studies, it was discovered that the floc volumes of suspensions increased on standing. As the floc volume and ultraclay have already been shown to increase together, it is very likely that increase in floc volume with time is due to corresponding increase in the ultraclay content. Dispersion of clay into ultraclay in that case would be a rather slow process.

The effect of aging was studied further on two soils, P. C. 13 and P. C. 142.

To 5-gm. portions of acid-treated soils, varying quantities of NaOH were added and the suspensions were shaken for 24 hours in the mechanical shaker. They were then diluted to 500 cc. in order to give a 1 per cent suspension, and their pH values were determined by means of the glass electrode. Thereafter the floc volume, clay content (<0.002 mm.), and percentage of ultraclay particles (<0.0001 mm.) were obtained. The determination of these values and of the pH values of all the suspensions was repeated after varying intervals of time. The results are given in table 3.

TABLE 3
*Effect of aging of soil suspension**

SUSPENSION NUMBER	pH					FLOC VOLUME					CLAY CONTENT					PARTICLES UP TO 0.0001 mm.†				
	0.1N NaOH added																			
	2 hours	26 hours	65 hours	90 hours	7 days	2 hours	26 hours	65 hours	90 hours	7 days	2 hours	26 hours	65 hours	90 hours	7 days	26 hours	65 hours	90 hours	7 days	
	cc.					cc.	cc.	cc.	cc.	cc.	%	%	%	%	%	%	%	%	%	
Soil P. C. 15 A. T.																				
1	0.5	7.1	7.05	6.95	6.95	0.05	0.07	0.08	0.08	0.08	9.8	10.5	11.2	11.4	11.4	3.4	4.7	5.3	5.4	
2	1.5	7.3	7.10	7.10	7.1	0.08	0.09	0.12	0.12	0.12	30.1	32.2	33.0	33.0	33.1	5.6	8.6	9.7	9.8	
3	2.0	9.0	8.40	8.3	8.3	0.20	0.30	0.41	0.43	0.43	40.2	43.2	43.1	44.0	44.2	17.1	26.3	27.2	27.3	
4	3.0	10.3	9.40	9.3	9.3	0.30	0.42	0.49	0.50	0.50	58.8	59.0	60.1	60.2	60.2	25.1	29.8	30.1	30.1	
5	4.0	10.7	9.7	9.6	9.5	0.48	0.65	0.70	0.70	0.70	64.0	63.5	63.6	63.8	64.0	32.1	36.5	36.5	36.6	
6	5.0	11.0	10.0	9.9	9.8	0.8	0.55	0.70	0.72	0.73	64.0	64.0	64.2	64.2	64.3	34.1	38.2	38.5	38.7	
7	6.0	11.4	10.35	10.2	10.2	10.2	0.65	0.73	0.73	0.74	64.0	64.8	65.0	65.1	65.1	36.1	38.3	38.8	38.8	
8	7.0	11.5	10.35	10.2	10.2	10.2	0.70	0.76	0.76	0.76	64.8	64.8	65.1	65.2	65.2	37.1	39.1	39.2	39.8	
9	8.0	11.6	10.35	10.3	10.2	10.2	0.71	0.76	0.76	0.76	64.6	65.0	64.8	65.2	64.8	37.2	39.3	40.0	40.1	
Soil P. C. 142 A. T.																				
1	0.5	7.0	6.90	6.85	6.80	6.80	0.05	0.07	0.08	0.08	0.08	12.1	12.3	12.5	12.7	13.0	4.1	5.0	5.1	5.1
2	1.5	7.6	7.5	8.4	7.3	7.3	0.09	0.12	0.13	0.13	0.13	25.7	26.1	26.7	26.8	26.8	6.8	8.2	8.8	9.6
3	2.0	8.8	8.3	8.2	8.1	8.1	0.20	0.32	0.39	0.41	0.41	40.2	40.3	40.2	40.3	40.3	16.1	17.1	25.1	25.5
4	3.0	9.2	9.0	8.9	8.8	8.8	0.28	0.38	0.46	0.48	0.48	50.1	51.1	51.3	52.0	52.0	20.1	23.1	28.1	28.1
5	4.0	10.8	9.9	9.7	9.7	9.7	0.57	0.62	0.63	0.63	0.63	62.0	62.1	61.9	62.3	62.5	28.1	30.1	31.1	31.2
6	5.0	11.0	10.1	10.0	9.55	9.55	0.61	0.65	0.65	0.66	0.66	62.8	62.4	62.5	63.0	63.0	30.0	31.2	31.2	31.2
7	6.0	11.2	11.1	10.0	9.55	9.55	0.65	0.68	0.69	0.69	0.69	63.2	63.5	63.5	63.6	63.6	32.0	33.0	33.0	33.1
8	7.0	11.4	10.3	10.2	10.1	10.1	0.65	0.69	0.70	0.70	0.70	63.2	63.1	63.2	63.2	63.1	33.2	33.9	34.0	34.1
9	8.0	11.5	10.5	10.2	10.1	10.1	0.66	0.69	0.70	0.70	0.70	63.0	63.0	63.1	63.1	63.2	34.1	34.6	34.2	34.2

* The time of shaking, 24 hours, is not included.

† As 24 hours' settling time is required to allow pipetting from the minimum depth of 1 mm., the value for 2 hours could not be obtained.

The following conclusions may be drawn:

As far as conventional clay is concerned, the various suspensions at different pH values acquire stable structure soon after 24 hours' mechanical shaking, for no appreciable increase in clay content is noticed up to 7 days' standing. Furthermore, the maximum dispersion on the basis of conventional clay is attained at pH 10.8-11.0.

The ultraclay (<0.0001 mm.), however, continues to increase in all cases up to 65 hours' standing reckoned from the end of the 24 hours' mechanical shaking. This happens even in suspensions at pH values higher than 11, though the effect is less pronounced. This

shows that ultraclay requires not only higher pH values than 10.8 but also a longer time than the usual 24 hours' shaking for complete dispersion. This will be readily understood if we assume that dispersion of soil takes place gradually, the coarser particles being resolved first, followed by the particles in the clay region, and then by those in the ultraclay region. After about 90 hours (including 24 hours of shaking), complete dispersion has taken place on the basis not only of conventional clay but also of ultimate primary particles in the truly colloidal region. Keeping the suspensions for a longer time than this does not produce any further change in ultraclay, and the suspensions acquire a comparatively permanent stable state.

The floc volume, like ultraclay content, increases with time of standing. The increase continues for as long as 65 hours in suspensions at lower pH values, but for only 26 hours in more alkaline suspensions, although ultraclay in the latter case increases to a small degree up to 65 hours. This apparent discrepancy will be readily resolved by reference to figure 5, in which the effect of concentration of ultraclay on floc volume is plotted. It will be seen that beyond a certain limit of ultraclay, the floc volume tends to become constant. This aspect is discussed in a subsequent section of this paper.

The pH value continues to decrease with time in all cases until it also becomes constant. This usually happens after 65 hours of standing, though the rate of fall gradually slows down. The explanation for the fall of pH value with time lies in the fact that the reaction between alkali and the acidoid takes place very slowly, as the soil particles exist in aggregates and the reactions involved take place only at the surface. When these aggregates, on contact with alkali, are gradually resolved, first, into smaller aggregates and then into ultimate primary units, fresh surfaces become exposed and the reaction continues if enough alkali is present. This will continue until hydrogen in the exchange complex is completely replaced by sodium. No further fall in pH value will then take place. As the maximum dispersion can take place only when the acidoid is completely converted into sodium saloid, the ultraclay particles continue to increase with the progressive increase of sodium in the exchange complex and attain constant value only when sufficient alkali is kept in contact with the acidoid long enough to complete this reaction.

CONTRIBUTION OF PARTICLES OF VARIOUS SIZES TO FLOC VOLUME

Although it appears that ultraclay particles determine to a large extent the volume of the flocculated mass, it is of interest to find out whether coarser particles also make a contribution toward this value and, if so, what is the magnitude of this contribution and at what particle size does it begin.

Two H-soils, with differently shaped size-distribution curves, were selected and dispersed by the addition of NaOH to raise their pH value to 11.0 and by shaking mechanically for 48 hours. Particles of various sizes were pipetted after appropriate times of settling and their floc volumes as well as their summation percentages were determined in the usual way. The results are given in table 4. It will be seen that particles coarser than 0.0001 mm. (10^{-5} cm.) do not make any material contribution to the floc volume. Particles finer than this, however, begin to affect this value to an increasing degree. It is interesting to note that although P. C. 13 contains only 27 per cent of particles below 0.00004 mm., these particles contribute 90 per cent toward the floc volume.

In order to determine the floc volume of any silica that might have gone into solution as a result of alkalinity of the medium, the two suspensions were filtered by means of Houston's pump and the floc volumes measured in the usual way by the addition of 1 cc. of 0.25 N CaCl_2 to 4 cc. of the filtrates. The flocculated

TABLE 4

Ultraclay as determined by the pipette method and by the flocculated volume method

SOIL NUMBER	FLOC VOLUME	ULTRACLAY					
		<10 ⁻⁵ cm. (0.0001 mm.)		<10 ^{-5.2} cm. (0.000063 mm.)		<10 ^{-5.4} cm. (0.00004 mm.)	
		Pipette method	Flocculated volume method	Pipette method	Flocculated volume method	Pipette method	Flocculated volume method
	cc.	per cent	per cent	per cent	per cent	per cent	per cent
116	0.11	6.9	6.0	4.0	4.35	3.1	3.5
117	0.04	3.2	2.37	1.7	1.50	1.2	1.30
118	0.15	8.3	7.87	5.2	5.60	4.5	4.27
119	0.38	20.2	16.3	11.4	11.0	9.1	8.8
120	0.06	4.0	3.25	2.5	2.15	2.0	1.80
121	0.05	3.6	2.80	2.5	1.80	1.7	1.50
122	0.04	3.0	2.37	1.6	1.50	1.3	1.30
124	0.04	2.9	2.37	1.5	1.50	1.4	1.30
125	0.06	4.5	3.25	2.5	2.15	1.8	1.80
126	0.22	11.3	11.00	7.4	7.10	6.1	5.75
127	0.18	10.0	9.12	6.0	6.32	4.9	5.25
128	0.08	6.2	4.06	2.5	2.80	2.2	2.20
129	0.26	13.3	12.5	8.7	8.12	6.8	6.50
130	0.23	10.8	11.50	7.5	7.36	6.0	5.92
132	0.22	9.7	11.00	7.2	7.10	5.6	5.75
133	0.18	7.8	9.12	5.8	6.32	5.0	5.25
134	0.04	2.5	2.37	1.4	1.50	1.2	1.30
135	0.05	2.60	2.80	1.5	1.80	1.2	1.5
136	0.10	6.0	5.50	3.3	4.0	2.8	3.0
137	0.10	5.8	5.50	3.2	4.0	2.65	3.0
138	0.20	9.1	10.0	6.1	6.72	5.7	5.5
139	0.08	5.1	4.06	3.0	2.8	2.4	2.2
141	0.42	19.8	18.00	13.5	12.7	9.9	9.7
142	0.55	31.1	30.50	22.1	20.2	15.8	16.3
144	0.13	6.7	7.0	4.3	5.0	3.75	4.2
149	0.27	12.4	12.8	9.01	8.40	6.83	6.66
152	0.06	4.1	3.25	1.5	2.15	1.36	1.80
153	0.14	6.6	7.50	4.5	5.30	3.72	4.50
159	0.13	6.2	7.0	4.5	5.0	3.4	4.20
160	0.10	5.1	5.50	3.9	4.0	2.5	3.00
163	0.11	5.2	6.00	4.0	4.35	2.9	3.69
165	0.30	14.0	13.75	9.4	9.00	7.1	7.30
166	0.19	9.8	9.56	6.3	6.52	5.2	5.37
167	0.06	3.0	3.25	2.1	2.15	1.6	1.8
168	0.08	3.3	4.06	2.6	2.80	2.0	2.20
169	0.06	2.9	3.25	2.2	2.15	1.8	1.80
172	0.33	15.0	14.65	9.8	9.66	7.7	7.81
173	0.08	3.2	4.06	2.6	2.80	2.13	2.2
175	0.11	5.3	6.00	4.1	4.35	3.0	3.65
177	0.04	2.5	2.37	1.8	1.50	1.51	1.30
181	0.20	9.7	10.00	6.8	6.72	5.6	5.75
182	0.04	2.5	2.37	1.7	1.50	1.5	1.30
183	0.08	3.5	4.06	2.5	2.80	2.3	2.20

TABLE 4—*Concluded*

SOIL NUMBER	FLOC VOLUME	ULTRACLAY					
		<10 ⁻⁶ cm. (0.0001 mm.)		<10 ^{-5.2} cm. (0.000063 mm.)		<10 ^{-5.4} cm. (0.00004 mm.)	
		Pipette method	Flocculated volume method	Pipette method	Flocculated volume method	Pipette method	Flocculated volume method
	cc.	per cent	per cent	per cent	per cent	per cent	per cent
184	0.13	6.3	7.00	4.5	5.00	3.5	4.20
221	0.07	4.6	3.65	2.5	2.47	1.7	2.00
222	0.18	9.5	9.12	6.0	6.32	5.1	5.25
223	0.11	6.6	5.20	4.2	4.00	3.1	2.90
224	0.16	10.0	8.25	5.7	5.90	4.7	5.0
226	0.13	6.2	7.00	4.8	5.00	3.2	4.20
227	0.11	7.0	5.20	4.4	4.00	2.9	2.90
229	0.20	11.0	10.00	7.2	6.72	5.2	5.50
230	0.15	8.2	7.87	5.1	5.60	4.5	4.77
231	0.17	12.0	8.68	10.4	6.11	6.9	5.12
232	0.17	12.4	8.68	10.2	6.11	6.0	5.12
233	0.25	12.0	12.25	8.2	7.87	6.5	6.30
234	0.20	16.6	10.00	7.5	6.72	5.9	5.50
245	0.16	9.2	8.25	5.4	5.90	4.7	5.0
246	0.32	14.8	14.35	9.2	9.40	8.0	7.64
249	0.20	9.7	10.00	6.8	6.72	5.6	5.50
291	0.11	9.5	5.20	3.7	4.00	3.00	2.90
Rawalpindi clay	0.07	3.1	3.65	2.6	2.47	3.6	2.00
13	0.58	41.0	40.0	30.7	27.0	27.0	22.0
15	0.10	7.0	5.5	5.1	4.0	3.2	3.0

mass was found to be absent altogether in P. C. 149. It had a negligibly small volume in P. C. 13, because of the presence of humus.

EFFECT OF CONCENTRATION OF SUSPENSION ON FLOC VOLUME

In order to study the effect of concentration on floc volume, four typical acid-treated soils were fully dispersed and clay was pipetted off in the usual way from 1 per cent suspensions. Different dilutions of each clay were prepared by taking 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4 cc. of the suspension and making to a volume of 4 cc. in each case with water. The floc volumes were determined as usual. The results are plotted in figure 4: 100 per cent concentration represents original clay without any dilution, 50 per cent represents the original clay diluted half and half with water, and so on. It will be seen from the results that floc volume does not increase in the same proportion as the concentration and that at a certain stage it becomes constant and quite independent of the concentration. This fact may be attributed to the mutual compression caused by the particles. As the concentration of the suspension increases, the force of compression also increases because of the increase in number of particles occupying the same space.

In figures 5, 6, and 7, the same results are plotted on the basis of the three ultra-

clay sizes (<0.0001 , <0.000064 , and <0.00004 mm.). The values plotted along the abscissas were obtained by dividing the percentages of various sizes

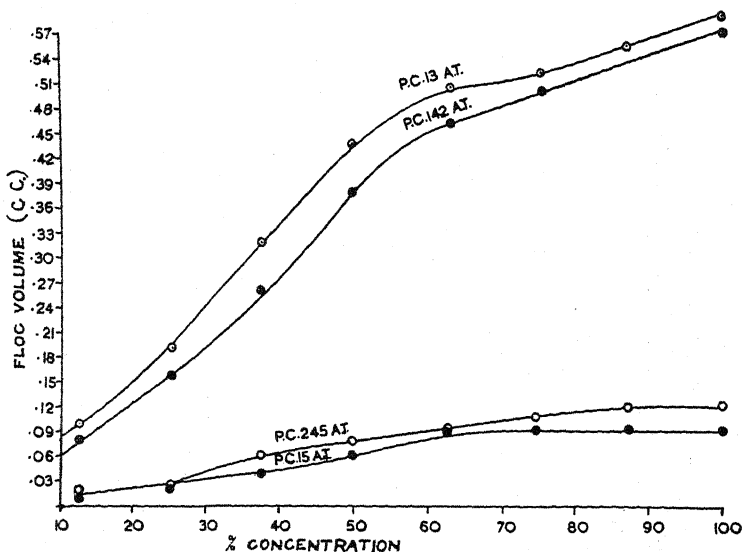


FIG. 4. EFFECT OF CONCENTRATION OF CLAY ON FLOC VOLUME OF SOILS

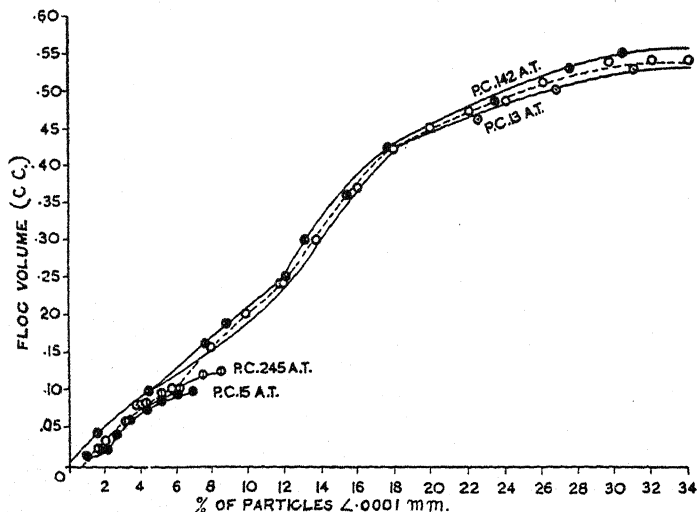


FIG. 5. RELATION BETWEEN FLOC VOLUME OF SOILS AND PERCENTAGE OF PARTICLES <0.0001 mm.

actually present in the soil by the number of times the clay was diluted. It will be seen that after a certain concentration of ultraclay particles is reached, the floc volume becomes constant.

Furthermore, all four curves for each of the three particle sizes (figs. 5, 6, and 7) have similar shapes. That all four curves for any particle size are not superimposed is to be expected, as it has already been shown that particles <0.0001

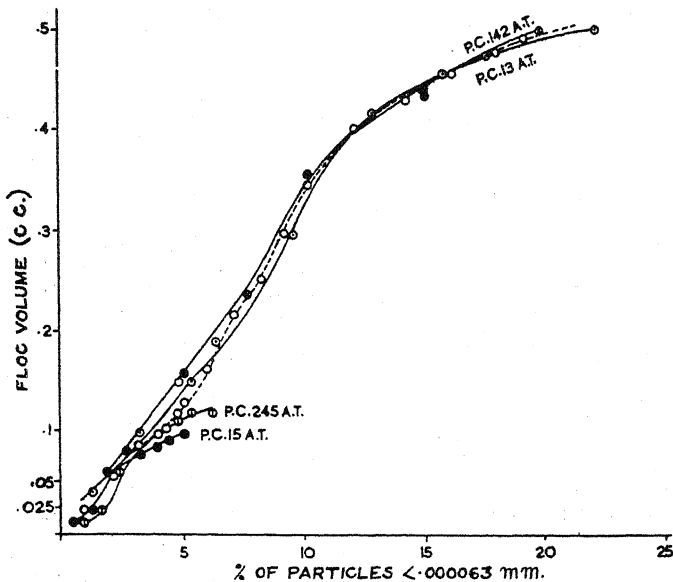


FIG. 6. RELATION BETWEEN FLOC VOLUME OF SOILS AND PERCENTAGE OF PARTICLES <0.000063 MM.

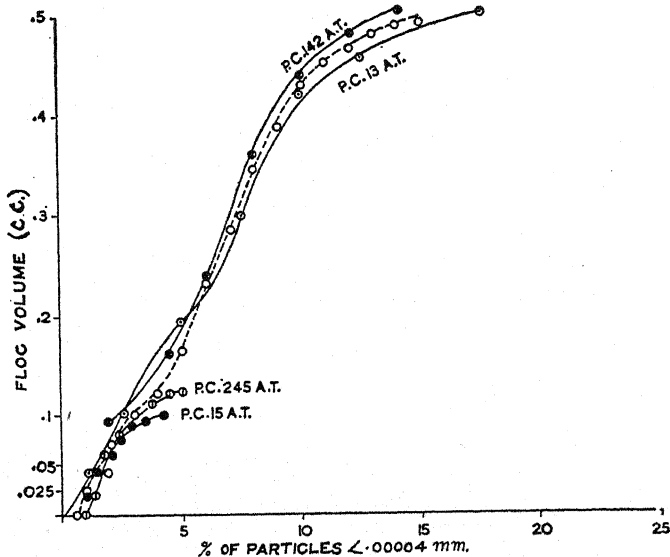


FIG. 7. RELATION BETWEEN FLOC VOLUME OF SOILS AND PERCENTAGE OF PARTICLES <0.00004 MM.

mm. do contribute to the floc volume, and when any two soils contain the same summation percentage of particles <0.0001 mm. diameter, it does not necessarily imply that their size distribution curves for various fractions below this size will be alike. The dotted curve in each figure was obtained by plotting mean values of ultraclay particles corresponding to various floc volumes. The mean curves may be used in calculating the percentages of various ultraclay particle sizes present in a suspension, as discussed in the following section.

ULTRACLAY PARTICLES AS DETERMINED FROM FLOC VOLUMES OF SOILS

Although it is not possible to determine with absolute accuracy, from knowledge of floc volume, the percentages of various fractions in the ultraclay region, a number of soils were studied to find out the degree of accuracy that can be attained. A method that would give readily within a few hours a fairly, if not absolutely, accurate measure of the percentages of particles of such fine dimensions as <0.000063 mm. obviously would be very helpful.

For this study, mean values of percentages of particles of various sizes (<0.0001 , <0.000063 , and <0.00004 mm.) corresponding to different values of flocculated volume were obtained from the mean curves plotted in figures 5, 6, and 7. All that need be done then is to find out the floc volume of a soil by the method outlined at the beginning of this paper, i.e., take 4 cc. of clay separated from 1 per cent fully dispersed soil suspension and determine its floc volume on the addition of 1 cc. of $0.25\text{ }N\text{ CaCl}_2$ followed by centrifuging for half an hour. The percentages of particles of various sizes can then be read on reference to the mean values.

This method was tested on 63 soils. The percentages of particles of all three sizes as determined by the micropipette technique and by the proposed method are given in table 4. The agreement is fairly close.

Thus the ultraclay fractions can be determined with a fair degree of accuracy by the proposed method. As no particular skill on the part of the observer is involved and determinations of such fine particles in a number of soils can be taken down within a few hours, the method has much to be said in its favor.

SUMMARY

A simple and rapid method of determining the floc volume of soils is described. It is shown to depend on the particle size in the ultraclay range.

The percentages of various ultraclay fractions present in a soil can be determined by measuring the floc volume of the soil.

Variations in pH value and in time of aging are shown to affect the floc volume as well as the ultraclay.

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ESTIMATION OF SOIL MOISTURE CONSERVATION FROM METEOROLOGICAL DATA¹

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This paper describes a method for estimating moisture conservation in fallow soil. The method applies in dry areas such as southwestern Saskatchewan where the conserved moisture can be taken as the difference between the recorded rainfall and the evaporation loss from the soil surface. Other losses such as those from runoff or subsoil drainage are disregarded.

In order to be of general use, a method for estimating moisture conservation must be based on the available meteorological data. Accurate daily rainfall records are necessary. Also, since vapor loss from the soil depends on the evaporating power of the atmosphere, records of evaporation from the free-water tank are required. If surface roughness and radiation effects are neglected, the loss from a saturated soil should be equal to the loss from a free-water surface. The actual loss from soil is usually much less than this because dry surface layers inhibit the upward movement of moisture. Thus the chief problem is to find how the rate of loss from soil falls off with the march of evaporation.

Evaporation of water from moist soil has been studied by Keen *et al.* (4, 5) and by Fisher (1, 2). Curves showing evaporation loss plotted against time usually have an initial constant-rate period followed by two different falling-rate periods. In its present state, such information does not permit one to predict what the evaporation will be in a given time under given conditions.

Geslin and Servy (3) developed a method whereby the moisture content to a depth of 18 inches could be calculated, given the initial moisture content and the evaporating power of the atmosphere as read by the Piché evaporimeter. The authors used the formula $E/E_s = f(H)$, where E was the evaporating power of the air, E_s evaporation from the soil, and $f(H)$ a constant function of H , the soil moisture content. Experiments conducted at Swift Current³ with 18-inch soil tanks failed to provide a unique $f(H)$ when percolation occurred below the surface layer. The top inch or two of soil dried out, and the rate of loss became equally slow for different values of H . Evidently the loss of water depends not only on the quantity but also on the location of the moisture within the soil mass.

Suppose a 5- to 8-inch depth of soil is moistened uniformly to field capacity

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³ SOIL RESEARCH LABORATORY 1938 ANNUAL REPORT. Dominion Experimental Station, Swift Current, Sask. (unpublished).

and then dried under simulated field conditions. After about a month the rate of loss becomes so slow that further loss can be neglected. If the soil is rewetted to field capacity and again dried, the rate of evaporation is found to be nearly the same as before. The same holds true when water is added in excess of field capacity, provided that evaporation is prevented until the excess is absorbed by the subsoil. This indicates that soil can be wetted and dried fairly reversibly between certain moisture limits. The quantity of water lost in each cycle may be termed "removable moisture" in the sense that it can be removed by evaporation. This removable moisture may be visualized as a quantity of water filling an open reservoir at the surface of the soil. If more rain occurs than is needed to fill the reservoir, the excess penetrates the soil beyond the evaporation zone.

Difficulty arises when rainfall fails to moisten the soil to field capacity. A dry layer is left below the surface—the reservoir appears to be full at the top but has lower compartments that are empty. Then, on evaporation, the initial loss is comparable to the field capacity rate, but the drier soil beneath soon fails to supply moisture and the rate falls off sharply. Thus as long as the soil is not wetted to field capacity, a different evaporation curve may be expected for each quantity of rainfall added. The number of different evaporation curves is further increased by the fact that the soil may not be thoroughly dried out when the rainfall occurs. Then after the rainfall, the dry layer may have removable moisture below it as well as above. The subsequent rate of evaporation depends on the amount of added moisture and on the shortage represented by the dry layer. The relation between these factors is determined in the experimental part of this paper.

EXPERIMENTAL METHODS

First it must be shown how experimentally measured values fit into the foregoing discussion. In actual experiment the initial moisture content was necessarily somewhat above the field capacity. It had to be established as near as possible to the average condition existing in field soils following a rain, and the field capacity is rarely attained before rapid evaporation commences. It was estimated that the required condition resulted within 3 hours after 1.0 inch of water was added to an air-dry soil. Thus, after a 3-hour period the soil was exposed to a fan in the laboratory, and the study of evaporation commenced.

Under the conditions of these experiments the loss of moisture became very slow after 4 weeks. The choice of a definite zero point for removable moisture was purely arbitrary. The only object was to choose a point so low that a field soil would not dry beyond it during a normal season. As will be shown later, the removable moisture was settled finally at 0.8 inch. This means simply that the total loss, after prolonged evaporation, will approach, but rarely exceed, 0.8 inch of water.

Evaporation loss was measured from columns of soil contained in metal cylinders 3.2 inches in diameter and 4.5 and 9.0 inches high. Forty short cylinders and eight tall cylinders were used. All were uniformly packed with air-dry soil. At the beginning, the short cylinders received 1.0 inch of water. This quantity would have wet the soil nearly to field capacity if equilibrium had been

established. Of the tall cylinders, the first pair received 0.5 inch of water, the second pair 1.0 inch, the third pair 1.5 inches, and the fourth pair 2.0 inches. After watering, all cylinders were left standing in a basement room for 3 hours. Then they were placed under a rotating, drum-shaped fan to evaporate. The platform beneath the fan was concave so that all evaporating surfaces were equidistant from the blades. Evaporation continued under the fan for approximately 8 hours daily throughout the experiment. For the remaining 16 hours the cylinders were left uncovered in a basement room where the evaporation was relatively slow. This procedure was intended to simulate day and night conditions. All containers were weighed each morning before the fan was started. The evaporating conditions of the atmosphere were found from the weights of cylinders of water placed beside the soil. In analyzing the results, losses from the soil were plotted against losses from the free-water surface.

All of the tall cylinders and one pair of the short cylinders evaporated without further addition of water for about 6 weeks. Of the others, after 1.5 days from zero time one pair received an additional 0.1 inch of water, a second pair received 0.2 inch, and a third pair 0.3 inch. After 3.5 days another pair received 0.2 inch, another 0.3 inch, and another 0.4 inch. Likewise after 5.5, 8.5, and 13.5 days different pairs of cylinders received additions of 0.2, 0.3, 0.4, and 0.5 inches of water. Following the last addition, the evaporation was continued for 4 weeks. By that time all cylinders had reached a low rate of loss.

RESULTS

In analyzing the data, the average losses from replicate pairs of cylinders were converted from grams to inches of water. Then the losses were subtracted from the maximum loss to give the removable moisture remaining in the soil. The point of maximum loss was considered reached at the end of 40 days. If the total loss was 0.82 inch and the loss in t days was E_t inches, the removable moisture at time t was $0.82 - E_t$ inches. This calculation was only temporary because some of the soils had not dried as thoroughly as the check samples. Variation in this respect was detected and the necessary adjustment made after the data were plotted.

The losses from the free-water cylinders were converted to their equivalent in losses from the standard meteorological tank. The conversion factor was obtained by a separate experiment in which the losses from cylinders of water were measured out of doors beside the standard tank. The cylinders were embedded in the soil so that the two water surfaces were at a common level. The depth of water lost from the cylinder was 1.6 times that lost from the tank. This daily ratio was fairly constant for a normal 16-day period in August. The small container followed closely the temperature of the soil, losing water rapidly during daytime. The tank, on the other hand, had a high heat capacity and lost much of its water at night. This method of relating laboratory and field evaporation losses is subject to many errors and can be justified only when put to practical test. All free-water losses referred to in the remainder of this paper are field-tank values or the equivalent in laboratory values divided by the factor 1.6.

A summary of the results is presented in table 1. The moisture contents of the

29-30	13.5	0.2	0.40																0.42	0.27	0.23	0.20	0.17	0.13																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
31-32	13.5	0.3	0.28																0.50	0.34	0.29	0.26	0.22	0.18	0.13																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
33-34	13.5	0.4	0.18																0.59	0.43	0.35	0.31	0.26	0.22	0.17																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
35-36	13.5	0.5	0.09																0.64	0.45	0.40	0.35	0.30	0.24	0.19																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
37-38	13.5	0.75	-0.19																0.87	0.66	0.49	0.41	0.34	0.27	0.20																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
Free-water																			0.00	0.15	0.32	0.52	0.88	1.24	1.97																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
39-40																			0.82	0.66	0.51	0.44	0.42	0.39	0.36	0.34	0.32	0.31	0.30	0.28	0.27	0.24	0.22	0.21	0.19	0.17	0.14	0.11																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
Free-water																			0.00	0.13	0.31	0.48	0.67	0.78	0.91	1.01	1.19	1.33	1.46	1.60	1.74	2.07	2.21	2.39	2.58	2.94	3.30	4.04																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
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11-12																			0.57	0.42	0.32	0.28	0.25	0.22	0.20	0.18	0.15	0.13	0.11																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																

* Initial water content of soil in short cylinders, 1 inch; in tall cylinders, nos. 11-12, 0.5 inch; nos. 17-18, 1 inch; nos. 24-25, 1.5 inches; nos. 31-32, 2 inches.

† Shortage calculated after water was added as indicated in column 3.

short cylinders are shown only after the different quantities of water have been added. Losses prior to this are assumed equal to the losses from check cylinders 39 and 40. The uniformity of the initial evaporation is shown by the agreement of the sum "additional water" plus "shortage from initial condition" (columns 3 and 4, table 1) for different pairs of cylinders.

The data from the tall cylinders (lower part of table 1) show striking differences in evaporation for the first 1.5 to 3.5 days as a result of different initial applications of water. No additional time had been allowed for the soils receiving the heavier applications to approach equilibrium, and they lost water for many hours at a rate approaching that from a free-water surface. If given sufficient time before evaporation starts, the water losses for applications of 1.0, 1.5, 2.0 inches would be more nearly equal than is shown in these experiments. The loss for 0.5 inch added water remains considerably below the others, in any case, because the moisture content is reduced rather rapidly to below the field capacity. The rate of loss following an application of 1.0 inch initial moisture is the standard used for the present study and will be referred to as the "standard curve." In southwestern Saskatchewan rainfalls of 1.5 and 2.0 inches are rarely followed by rapid evaporation; therefore, the corresponding high losses shown in the table are uncommon under field conditions.

The results for the short cylinders (upper part of table 1) were sorted out by plotting the data for different quantities of added water on separate sheets. For instance, the addition of 0.2 inch of water to soil at different moisture contents was represented by the standard curve (cylinders 39-40) plus five secondary curves (cylinders 3-4, 7-8, 13-14, 21-22, 29-30). The removable soil water content was plotted against the free-water loss, the peak value for each of the six curves commencing at a common origin. Allowance had to be made in plotting the data for additions of 0.3, 0.4, and 0.5 inches because these heavier applications had not dried sufficiently when the trial ended. Also, some adjustment was necessary in a few cases where water had escaped through cracks in the soil beyond the evaporation zone.

The final experimental results were in the form of four figures representing additions of 0.2, 0.3, 0.4, and 0.5 inches of water. Considered in terms of field conditions, each figure traced the evaporation of water from soil following a certain rainfall when the soil was at different moisture contents initially. Given the initial removable moisture content, rainfall records (accurate to 0.1 inch), and free-water evaporation data, the curves should be adequate for estimation of the removable moisture content continuously throughout the season. They were found difficult to use, however, because their peak values were not uniformly distributed along the removable moisture axis. It was necessary, therefore, to draw new curves by interpolation in order to have the initial removable moistures or shortages vary in even steps of 0.1 inch. These curves appear in figure 1. The general shapes of the experimental curves were retained as far as possible. Greater uniformity was introduced in the interpolation when it was noted that the free-water evaporation during the loss of a rainfall of R inches, with a shortage of S inches, was $R/(R + S)$ times the free-water evaporation during the loss

of $(R + S)$ inches of moisture with no shortage. In other words, if the rainfall was 0.2 inch and the shortage 0.1 inch, the free-water evaporation needed to lose

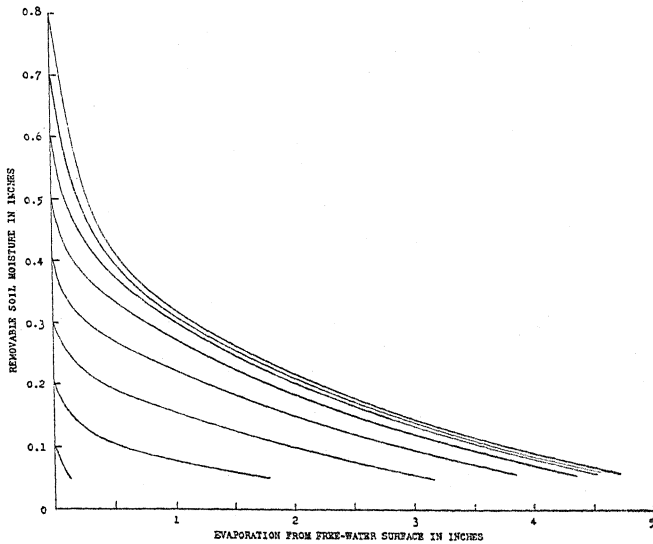


FIG. 1a. EVAPORATION CURVES FOR RAINFALL OF 0.1 INCH
The shortage equals 0.8 inch minus the removable moisture

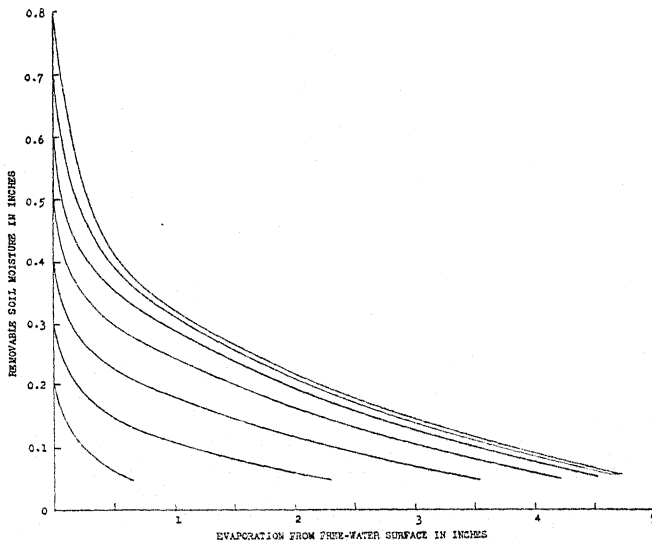


FIG. 1b. EVAPORATION CURVES FOR RAINFALL OF 0.2 INCH

the rainfall was two-thirds the evaporation needed to lose 0.3 inch along the standard curve. Table 2 shows to what extent this rule holds for the experimental data. The shortages are based on the minimum reached at the end of the

trial, without correction for the small quantity of removable moisture retained by the more heavily watered soils. On the basis of the results for only 0.2 and 0.3 inches of rainfall, there is a tendency for the ratio of calculated to measured

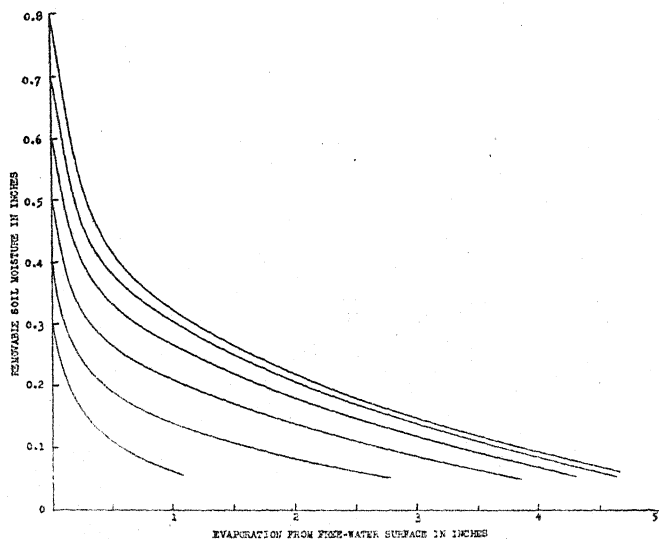


FIG. 1c. EVAPORATION CURVES FOR RAINFALL OF 0.3 INCH

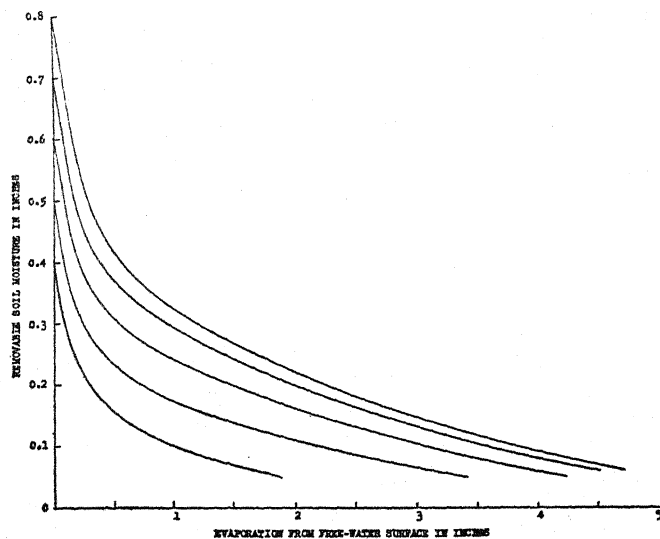


FIG. 1d. EVAPORATION CURVES FOR RAINFALL OF 0.4 INCH

values to increase with shortage. Nevertheless, the calculation shows satisfactory agreement over most of the range. By using the proposed method of interpolation, the curves of figure 1 were drawn in with greater uniformity, and yet retained essentially the same shape and magnitude as the experimental curves.

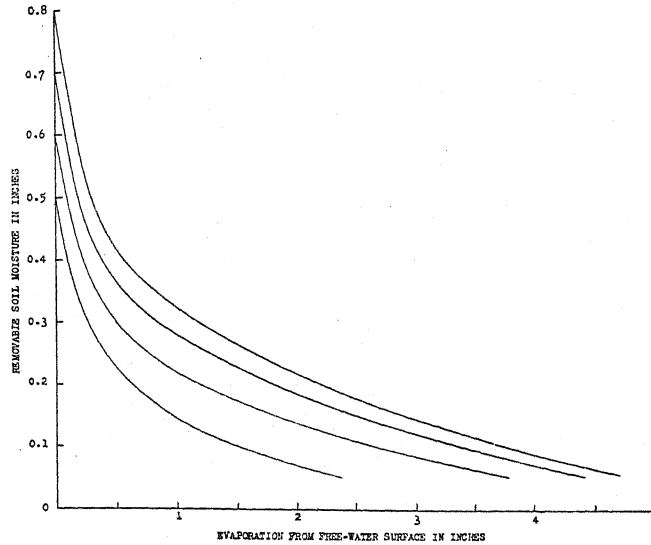


FIG. 1e. EVAPORATION CURVES FOR RAINFALL OF 0.5 INCH

TABLE 2

Effect of rainfall and shortage on relative evaporation from soil and free-water surface

RAINFALL (R)	SHORTAGE (S)	R + S	FREE-WATER EVAPORATION WHILE SOIL LOST R + S INCHES (STANDARD CURVE)	FREE-WATER EVAPORATION WHILE SOIL LOST R INCHES, SHORTAGE S	
				Calculated*	Experimental
<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>
0.2	0.12	0.32	0.32	0.20	0.21
0.2	0.22	0.42	0.67	0.32	0.32
0.2	0.28	0.48	0.99	0.41	0.43
0.2	0.34	0.54	1.50	0.56	0.58
0.2	0.41	0.61	2.33	0.76	0.70
0.3	0.13	0.43	0.70	0.49	0.55
0.3	0.19	0.49	1.10	0.67	0.77
0.3	0.25	0.55	1.63	0.89	0.88
0.3	0.33	0.63	2.55	1.22	1.07
0.4	0.10	0.50	1.18	0.94	1.12
0.4	0.16	0.56	1.72	1.23	1.25
0.4	0.23	0.63	2.66	1.69	1.65
0.5	0.09	0.59	2.06	1.75	1.67
0.5	0.18	0.68	3.45	2.53	2.53

$$\frac{R}{R + S} \times \text{column 4.}$$

From a comparison of the different rainfall groups of figure 1, it appears that the differences become less and less pronounced as the added water increases. This could be expected, since, with increase of water, a given shortage becomes

farther removed from the surface. There is very little difference between the curves for additions of 0.4 and 0.5 inches.

Another interesting feature is that the curve for a shortage of 0.1 inch almost coincides with part of the standard curve, the upper curve in each graph. This is understandable when it is noted that for the upper 0.2 to 0.3 inches the standard curve is almost a straight line. Presumably this line represents the loss of moisture that is not held by strong forces and is rather mobile. Thus the curves for rainfalls of 0.1 and 0.2 inches, and shortage of 0.1 inch, are little different from the standard curve with 0.1 inch removed at the top. The same holds true, though to a lesser extent, for shortages of 0.2 inch. But on reaching a shortage of 0.3 inch the curves are very different from one another and from the standard curve beginning at the same level. It is very doubtful whether a true constant-rate zone extends more than 0.25 inch below the peak of the standard curve. The steepness of the experimental curves during their initial stages makes it difficult to decide this point.

PRACTICAL APPLICATION OF THE EVAPORATION CURVES

Figure 1 shows the loss for nearly all moisture conditions likely to occur. With the help of these curves it is possible to trace continuously the rise and fall of the removable moisture. It is necessary to start when the surface moisture condition is fairly well known—for instance, in the springtime just after the snow has disappeared and the reservoir of removable moisture remains filled.

Then the soil moisture content may be traced along the standard curve until rainfall occurs. The distance of travel along the curve is determined by an interval on the abscissa equivalent to the recorded free-water evaporation for the period. The moisture content and rainfall need be read only to the nearest 0.1 inch. Suppose, for example, the soil has dried down to 0.23 inch removable moisture when a rainfall of 0.44 inch occurs. The moisture content is taken as 0.2 inch and the rainfall as 0.4 inch, leaving a net shortage of 0.2 inch. With subsequent evaporation, the loss will be shown in figure 1d along the curve for a shortage of 0.2 inch. Then after more rainfall the process will be repeated as before, each curve being followed down for an interval corresponding to the free-water evaporation between successive rainfalls. In this way a continuous record of removable moisture may be obtained.

Any rainfall in excess of the 0.8 inch removable moisture is recorded as conserved. Some modification of this rule must be made when very low evaporation follows abundant rainfall, *viz.*, rainfall which wets the soil to the 0.8-inch level or higher. The standard curve is based on evaporation commencing shortly after rain occurs. If 24 to 36 hours of very slow evaporation intervenes, the soil approaches field capacity and the removable moisture is reduced. To allow for this, the soil is estimated to contain only 0.6 inch of removable water within 36 hours after a rainfall wetting to 0.8 inch. Thus additional moisture is conserved if, on the day following a rain, the evaporation from the soil is less than 0.2 inch. As an example of the foregoing, suppose a soil containing 0.6 inch moisture receives a rainfall of 0.3 inch. The 0.1 inch excess water can be

written down immediately as conserved. The standard curve is used to trace the loss on the following day. If the free-water loss is so high that the soil loses more than 0.2 inch of water, the curve can be followed down as usual to the next rainfall. But if the loss from the soil on the second day is only 0.1 inch, a further conservation of 0.1 inch (0.2-0.1) must be recorded. On the third day evaporation commences on the standard curve at the 0.6-inch level. Some allowance must be made in reading the evaporation interval because at 0.6 inch the curve is displaced from the vertical axis.

TABLE 3
Moisture conservation in fallowed tanks

YEAR	PERIOD	RAINFALL	EVAPORA- TION	ESTIMATED CONSERVATION		MEASURED CONSER- VATION
				Method A	Method B	
		<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>
1922	June 1 to Aug. 21.....	7.98	15.34	3.0	3.1	2.6
1923	May 15 to Nov. 1.....	14.43	22.75	7.1	7.0	4.8
1924	May 16 to Oct. 21.....	11.61	23.86	4.2	4.9	4.8
1925	May 12 to Nov. 2.....	7.97	24.66	1.8	1.3	1.9
1926	May 12 to Oct. 30.....	10.51	24.94	2.4	2.5	2.5
1927	May 16 to Nov. 1.....	13.93	22.68	5.8	4.9	5.8
1928	May 21 to Sep. 10.....	8.47	26.13	3.2	3.0	3.1
1929	May 7 to Aug. 10.....	7.76	34.93	2.0	2.6	2.6
1930	May 5 to Oct. 23.....	9.10	32.39	3.8	3.6	3.5
1931	May 16 to Oct. 31.....	7.22	34.70	2.2	2.0	2.3
1932	May 9 to Nov. 5.....	12.14	27.31	5.0	4.8	4.4
1933	May 11 to Nov. 2.....	10.33	31.34	3.6	3.2	3.6
1934	May 23 to Oct. 30.....	8.07	30.81	2.1	2.1	1.5
1935	May 16 to Sep. 15.....	6.70	23.20	2.0	2.1	2.3
1936	June 3 to Oct. 27.....	5.55	30.72	1.3	1.3	0.8
1937	May 19 to Nov. 3.....	4.78	37.08	0.2	0.1	0.1
1938	May 9 to Oct. 18.....	8.13	32.40	1.7	2.1	1.2
1939	May 11 to Oct. 19.....	11.86	26.13	6.2	5.9	5.3
1940	May 3 to Oct. 30.....	7.45	35.60	1.7	2.1	0.8
1941	May 1 to Nov. 12.....	8.35	36.08	1.0	1.4	0.9

Data from tank experiments conducted at this station during the years 1922 to 1941 provide a convenient check on the evaporation curves in figure 1. The tanks used in these experiments were 15 inches in diameter and 5 feet deep. They were set in pits so that the surface of the soil was level with the surrounding plot. The data in the original form consisted of the weights of fallow tanks recorded at intervals throughout the summer months. For the present purpose, the gain or loss in weight during each interval was changed to inches of water. Evaporation from the free-water surface was calculated for the same intervals. Rainfall data were retabulated to read to the nearest 0.1 inch.

A summary of these data with estimated moisture conservation is presented in table 3. The method of estimation discussed thus far comprises method A of the table. Method B was very similar except that the intervals in days between

TABLE 4

Detail used in estimating the moisture conserved in fallowed tanks in 1939

DATE	DAYS SINCE LAST RAIN	RAINFALL		EVAPORA- TION	CALCULATED CONSERVATION			MEASURED CONSERVA- TION
		Measured*	Nearest 0.1 inch		Percolated moisture	Surface moisture	Total conserved	
		<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>
May 5	11	0.09	0.1	0.95				
11	6			1.16†		0.2		
19	14	1.38	1.4	3.04	0.7			
20	1	0.44	0.4	0.00	0.2			
21	1	0.12	0.1	0.03	0.4			
22	1	0.67	0.7	0.00	0.8			
24	2	0.16	0.2	0.07				
25	1	0.05	0.1	0.02	0.1			
30	5			0.90		0.3	2.3	2.4
31	6	0.38	0.4	1.37				
June 4	4	0.10	0.1	0.71				
5	1	0.56	0.6	0.00	0.2			
6	1	0.37	0.4	0.16	0.2			
7	1	0.20	0.2	0.08	0.1			
8	1	0.18	0.2	0.11	0.1			
9	1	0.45	0.5	0.00	0.4			
13	4	0.56	0.6	0.57	0.2			
15	2	0.26	0.3	0.23	0.2			
16	1	0.71	0.7	0.00	0.7			
17	1	0.25	0.3	0.00	0.3			
18	1	0.62	0.6	0.00	0.6			
19	1	0.34	0.3	0.00	0.1			
20	1	0.61	0.6	0.22	0.4			
21	1	0.06	0.1	0.14				
23	2	0.35	0.4	0.18				
23	0			0.30		0.5	3.7	3.4
24	1	0.21	0.2	0.11	0.2			
25	1	0.07	0.1	0.06				
July 1	6	0.06	0.1	1.11				
3	2	0.07	0.1	0.34				
7	4	0.19	0.2	0.75				
15	8	0.34	0.3	1.99				
18	3			0.61		0.2	-0.1	-0.2
20	5	1.15	1.2	1.25	0.5			
Aug. 1	12			2.47		0.2	0.5	0.2
6	17	0.10	0.1	3.89				
8	2	0.07	0.1	0.24				
28	20	0.08	0.1	4.81				
30	2			0.35		0.0	-0.2	-0.3

TABLE 4—*Concluded*

DATE	DAYS SINCE LAST RAIN	RAINFALL		EVAPORA- TION	CALCULATED CONSERVATION			MEASURED CONSERVA- TION
		Measured*	Nearest 0.1 inch		Percolated moisture	Surface moisture	Total conserved	
		<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>
Sept. 1	4	0.05	0.1	1.04				
12	11	0.05	0.1	2.15				
23	11	0.06	0.1	1.83				
Oct. 1	8	0.14	0.1	0.57				
9	8	0.06	0.1				
12	3	0.07	0.1				
19	7					0.0	0.0	-0.2
21	9	0.06	0.1					
24	3	0.31	0.3					
27	3	0.06	0.1					
							6.2	5.3

* Rainfall less than 0.05 inch omitted.

† Evaporation is summed past the underlined values, since these appear on dates when tanks were weighed, not necessarily when rain fell.

rainfalls were used to estimate loss in place of the measured free-water evaporation. The average daily evaporation for the different months was used to make the abscissa of the evaporation curves read directly in days. This method was tested to see whether moisture conservation could be calculated when average, but not detailed, evaporation data were available. The approximate average daily evaporation for May, June, and August was 0.2 inch; for July, 0.24 inch; for September, 0.14 inch; and for October, 0.075 inch.

The detail of the computation (method A) for the year 1939 is shown in table 4.

DISCUSSION

The agreement between estimated and measured conservation is considered satisfactory for practical purposes. This result, along with the fair agreement between methods A and B, show that many of the possible complicating factors in evaporation are of little consequence when soils are exposed to natural conditions. This applies particularly to evaporation in dry weather when the removable moisture is low and the rate of loss is negligible over long periods. The rate of loss is very sensitive to free-water evaporation for only a short time after a rain, and any differences in loss occurring during this period are erased if many days pass before the next rainfall.

A few of the possible errors in the use of method A are listed below:

a. The most obvious error is found in the assumption that only 0.8 inch of moisture is lost by evaporation from a soil moistened initially to near the field capacity. This is but an arbitrary limit and experiment shows that further loss takes place, though at a very slow and almost constant rate, until another 0.3 inch or more of moisture is lost. This

error occurs in the calculation for very dry years such as 1936, 1937, and 1938. During these years the evaporation from free-water frequently exceeded the range of the calibration curves.

b. It is assumed that the soil is moistened, immediately following a rain, to a condition corresponding to the standard curve. This curve, however, is not unique, but is close to the mean value that would be obtained if likely rainfalls and likely subsequent intensities of evaporation are considered. The possible error increases with the amount of rainfall in excess of the 0.8-inch surface moisture. Also, the error can be large in the other direction if the final rainfall bringing the quantity up to 0.8 inch is very light, or falls over a long period. Fortunately these errors are partly compensated by the fact that, except in the case of heavy thunder showers, the period of cloudy weather immediately following a storm is roughly proportional to the precipitation received. Thus, quite automatically, the heavy rainfall is given time to approach equilibrium under reduced evaporation, whereas following a light shower the evaporation is generally rapid. These characteristics of normal rainfall tend toward a mean evaporation curve corresponding to a moisture condition somewhat above the field capacity.

That the error involved here is small is evidenced by the fact that the present method gave satisfactory results for such wet seasons as 1927 and 1939.

c. The use of a single set of evaporation curves as in figure 1 implies that evaporation from soil varies with the total loss of water from the free-water tank, thus being independent of fluctuations in daily rate. This is strictly true only when the removable moisture is less than 0.6 inch. The discussion in section b emphasizes the error involved if the soil is unusually moist when evaporation commences. Likewise, even when the removable moisture content is reduced to 0.8 inch, a slow redistribution of moisture within the soil continues, and the vapor loss may be less than predicted by the curves if the weather is damp for the first day or so after the rain. This possibility made necessary the rule used in the calculations whereby the removable moisture was estimated at 0.6 inch within 36 hours after a rain, whether or not there was loss through evaporation. The modified procedure gives an approximation to what actually occurs and improves the agreement with measured conservation.

The solar radiation effect mentioned in section e is, of course, a special case where a rapid initial evaporation reduces rather than increases the loss from soil.

d. The factor transferring from laboratory to field data introduces some error. Radiation effects are uncertain because of the differences in heat capacity of the surfaces involved. Also, water loss from a laboratory cylinder is not strictly proportional to surface area when the evaporating surface is moistened to near saturation. The situation is so complicated that one would be justified in choosing the scale that gives the best result.

e. The mulch-producing power of direct sunlight is another possible source of error. Radiation effects were ignored in this work, as the experiments were conducted indoors under constant temperature conditions. Penman (6) has shown that direct insolation produces a rapid initial loss followed by a much lower rate, and that the net result is reduced evaporation. Undoubtedly this causes appreciable error in our calculations on some days, particularly after heavy rains when rapid mulch formation would reduce surface evaporation and give the excess moisture time to penetrate beyond the surface. With moderate to light rainfall, however, the effect should be likened to the usual dryland dust mulch which has proved ineffective over long, dry periods. Furthermore, from Penman's paper, it seems possible that his soils were held under stress of evaporation continually throughout the experiment. A dry crust once formed would remain a barrier to moisture movement. In the present laboratory experiments the evaporation was made intermittent in an attempt to simulate outdoor conditions. During the early stages of evaporation, when the radiation effect applies, soil surfaces that were dry at night were found moist next morning. In fact, a fairly large percentage of the loss from the soils took place at night when the loss from free water was small.

SUGGESTIONS FOR GENERAL USE

The possible effect of different soil textures on evaporation has been disregarded in the foregoing discussion. A uniform loam soil with a moisture equivalent of 22 per cent was used in all experimental work. This soil is representative of many large areas throughout southwestern Saskatchewan. It is expected, of course, that soils of different textures will have different evaporation curves, but for practical purposes it is believed that two or three sets of curves may cover all types of soil satisfactorily. Tank experiments show that medium- and fine-textured soils differ less in vapor loss than is generally believed. A loam soil

TABLE 5
Moisture conservation on fallowed plots at Swift Current, Saskatchewan

YEAR	PERIOD	RAIN- FALL	EVAPO- RATION	ESTI- MATED CONSER- VATION METHOD A	MEASURED CONSERVATION*		
					Plot 1	Plot 2	Average
		inches	inches	inches	inches	inches	inches
1924	May 26 to Sep. 18	7.19	19.66	0.9	-1.4	1.1	-0.2
1926	May 27 to Sep. 27	8.34	20.33	2.3	3.1	0.7	1.9
1928	May 26 to Sep. 13	7.80	20.10	3.3	3.8	3.3	3.6
1929	May 16 to Sep. 16	6.44	29.68	1.8	1.0	1.6	1.3
1930	May 16 to Sep. 19	6.31	29.16	2.4	1.7	0.4	1.1
1931	May 15 to July 16	2.92	16.03	0.6	0.7 [1.0]	0.8 [0.7]	0.8 [0.9]
1932	May 16 to July 18	6.64	11.44	3.5	2.9 [3.1]	3.4 [3.9]	3.2 [3.5]
1933	May 26 to Aug. 11	3.67	20.35	0.2	-1.1 [-1.0]	-1.6 [-1.7]	-1.4 [-1.4]
1934	May 14 to Aug. 9	6.08	21.94	1.7	1.4 [1.5]	0.8 [0.5]	1.1 [1.0]
1935	May 23 to July 15	4.81	9.88	1.6	0.7 [1.8]	1.0 [1.1]	0.9 [1.5]
1937	May 19 to Oct. 21	4.66	37.08	0.3	0.6	0.7	0.7
1938	May 24 to Oct. 17	7.83	29.42	1.9	1.8	1.7	1.8
1939	May 30 to Oct. 16	9.03	23.23	3.6	1.6	1.5	1.6
1940	May 6 to Nov. 7	7.78	35.33	1.8	0.7	2.3	1.5
1941	May 9 to Oct. 14	7.98	33.82	0.9	0.7	0.8	0.8

* Figures in brackets obtained in correcting for soil heterogeneity by the moisture-equivalent method.

is frequently dried to a greater depth than a clay, but because of the difference in water-holding capacity, both types lose roughly the same amount of water.

It is intended that the method described herein be checked thoroughly in the field, conservation being based on samples taken from different soil types. A limited number of data are already available from yearly sampling of field plots and strips at the Dominion Experimental Station, Swift Current. These data are presented with the corresponding estimated moisture conservations in table 5. The plot results extend over almost the same period of years as the tank results (table 3), but the number of days per year differs in each case.

The agreement between estimated and measured conservation is considered satisfactory. The plots were maintained under much less ideal conditions than

were the tanks, and frequently lower conservation resulted. The data from two plots per year have been included in order to show the variation obtained. Weed growth contributes most to this variation, as well as to the difference between plots and tanks. The tanks were kept free of weeds, whereas the plots sometimes became weedy between cultivations, particularly during wet seasons when field cultivation was impossible. This accounts for much of the difference between calculated and measured conservation in 1939 (table 5). The plots were also affected more by runoff and soil heterogeneity than were the tanks. The results in brackets (columns 6, 7, and 8, table 5), obtained by correcting for soil heterogeneity, show that this error was usually small.

The computations are straightforward for a station where both rainfall and evaporation are recorded. At stations and country points where evaporation data are not available, it is believed that evaporation from a few centrally located stations, used with the local rainfall, may give fair accuracy. The satisfactory agreement of methods A and B, table 3, suggests that detailed evaporation records are not needed.

For general use it is suggested that the curves of figure 1 be placed side by side on a board with a cursor attached (slide rule style). The cursor should carry an index pointer for vertical travel. In this way the pointer can follow any curve, showing always the moisture content and the current rate of loss from the surface soil. Moisture conserved below the surface should be recorded on a mimeographed sheet after the form of table 4.

SUMMARY

Soil moisture conservation is estimated by application of the familiar concept that the surface soil must be moistened to its field capacity before water will penetrate to the subsoil. In the present work the surface soil at field capacity is likened to a full reservoir with a constant volume equal to that occupied by 0.8 inch of water. As a starting basis, the reservoir is considered full when an air-dry loam soil receives 1.0 inch of rainfall, and empty (arbitrarily) when 0.8 inch of this moisture is removed by evaporation. Once the surface soil is filled, additional rainfall percolates downward out of reach of evaporation. Runoff is disregarded.

The removable moisture in the surface soil may be found with the help of experimentally determined evaporation curves in which removable moisture is plotted against evaporation from the standard free-water tank. Each curve starts with the removable moisture present immediately after a rain, and traces the evaporation until the arbitrary zero point is reached. When a rainfall does not fill the reservoir, a shortage exists and the initial moisture content is correspondingly reduced. Furthermore, for each initial moisture content, the shape of the evaporation curve is determined by the amount of the recent rainfall. Separate curves are provided for all combinations of rainfall and removable moisture (in units of 0.1 inch) likely to occur in the wetting and drying of field soils.

In dry years the surface soil is rarely filled; there is usually a large shortage,

and the removable moisture merely oscillates up and down with alternate wetting and drying. During wet years, on the other hand, frequent showers keep the surface moistened to near the field capacity and a relatively large percentage of the rainfall is conserved.

The evaporation curves are used to calculate the moisture conservation in fallow soils for the years 1922 to 1941. The results are in satisfactory agreement with measured conservations both in soil tanks and in plots.

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OXIDATION LOSS OF LOWMOOR PEAT IN FIELDS WITH DIFFERENT WATER TABLES

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That a high concentration of carbon dioxide occurs in the soil air of lowmoor Everglades peat when a water table is maintained low enough to permit the use of the land crops is shown in another paper (5). It is suggested that this high concentration of carbon dioxide between the root zone and the water table level probably functions as a protecting blanket to keep the roots from going too deep and becoming waterlogged when the water table is raised by heavy rains and before the pumps can remove the excess water.

Clayton, Neller, and Allison (4) point out that water control by means of pumps is necessary for the farming of Everglades peat. They also record the effect of partial or gravity drainage upon the subsidence of areas of peat not yet in cultivation, and show that the loss in elevation in these undeveloped areas may be less but the actual loss of peat is greater because the density of the surface layers is considerably less than in similar peatland that is under water control for agricultural use. Inasmuch as the peat is underlain with limestone, it is a matter of high importance to reduce the rate of subsidence as much as possible, thereby prolonging the useful agricultural life of the peat.

Oxidation losses may be expected to be heavy in peats that have been drained to the extent that the accumulated masses of partly decomposed material are exposed to aeration. For a given amount of drainage, the amount of oxidation depends on the type of peat, which in turn has been determined by the climatological conditions under which the peat was formed and to which it is likewise subjected after drainage. Clayton, Neller, and Allison (4) describe these factors for the Everglades peat, and the present paper records the experiments designed to ascertain the part that oxidation is playing in the diminution of the surface of the peat.

The surface layers of Everglades peat that have been placed under water control have pH values of 5 to 6, which increase to and beyond 7 in the deeper layers because of the limestone rock that lies immediately beneath. The ash content ranges from 10 to 15 per cent, and the volume weight from 10 to 18 pounds per cubic foot, oven dry basis. Diffusion processes are doubtless rapid in the drained layers, at least as far down as the plastic layer about 18 inches below the surface. These and other characteristics of the peat were described several years ago by Allison, Bryan, and Hunter (1).

EXPERIMENTAL

In 1934 a field of Everglades peat was divided into eight blocks, each 100 by 240 feet (2). These are surrounded by a system of ditches and check dams for the

¹ L. S. Jones assisted with the collection and analysis of samples.

conduction of soil waters whereby the water table is held at a different level in each block. This is accomplished by means of electrically operated pumps under automatic control which pump the water from the block of deepest water table to that of the highest, from which it passes over check dams successively to each of the lower levels. Mole drains were installed in all of the blocks to aid in maintaining more constant water levels. The prescribed water table levels were established in November, 1935.

Figure 1 is a general view of these fields with the pump house in the middle background. Shelters to house the recording instruments, one for each field, may also be seen. The photograph was taken August 20, 1934, when the fields were all being held at the same water level and were being uniformly cropped to determine field variability.

The purpose of the water table experiments was twofold: one, to determine the effect of water level on the subsidence of the peat and its loss by oxidation; and the other, to study the effect of different water levels on the growth of various crops.

During February to May, 1936, equipment was designed and installed on several of the fields for the purpose of measuring the amount of oxidation of the peat *in situ* as related to water table level. Each unit of this equipment consisted of a thin brass cylinder, 4 inches in diameter, which was pushed down into the peat far enough to insure that the lower end was beneath the water table. By sharpening the lower end of the cylinder and inserting it with a twisting motion it was possible to install it without compacting the enclosed column of peat appreciably. The top of the cylinder (fig. 2) was then closed by soldering on a cap which carried the outlet and inlet tubes. The outlet tube extended down into the peat to a point midway between the water table level and the surface of the peat, whereas the inlet tube stopped at the surface.

Aeration of the enclosed peat and collection of the carbon dioxide produced therein was accomplished by aspirating a measured amount of air into and out of the cylinder through flasks containing a solution of sodium hydroxide of known normality. The arrangement is shown in figure 2. Suction was obtained by water displacement from the upper to the lower bottle. At the end of a collection period the inlet and outlet tubes of the soil cylinder were closed and the flasks of sodium hydroxide were capped and taken to the laboratory for determination of the carbon dioxide by titration. An addition to the equipment, not shown in figure 2, was a latticed cover for the cylinder and surrounding soil to prevent the rays of the sun from heating the cylinder and conducting heat to the cooler subsurfaces. The pipe extending from the ground at the left is connected to a container for the collection of samples of soil air as described in a previous paper (5).

Since temperature of the peat is a basic factor controlling the rate and amount of oxidation, soil thermographs of the type shown in figure 3 were installed in the fields with the 12- and 36-inch water tables. The average diurnal temperature (5) $3\frac{1}{2}$ inches below the surface was the same (about 80°F.) for both fields from March through May. It was slightly higher at the $3\frac{1}{2}$ -inch level over the 12-inch

water table from June through November. From December through February an average temperature of 69° was recorded for the $3\frac{1}{2}$ - and 7-inch levels as well as for the air above the surface of the peat.

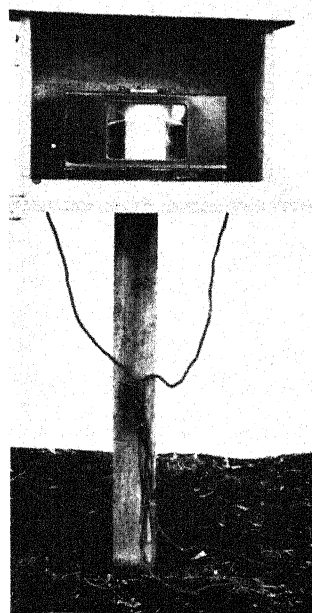
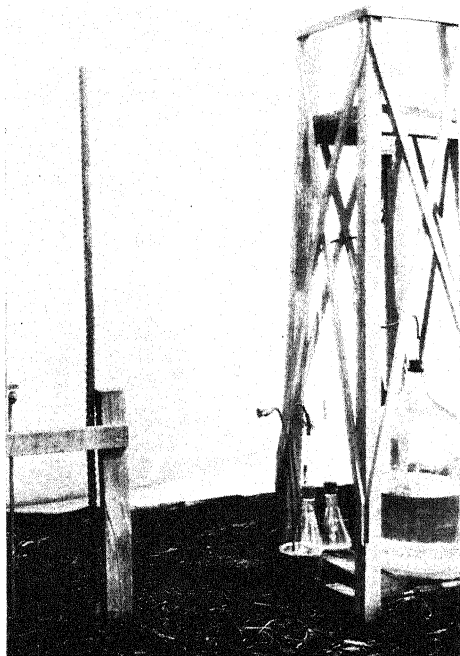


FIG. 1. (Top.) GENERAL VIEW OF THE WATER TABLE FIELD

The 12, 18, 24, 30, 36 and 36 variable water tables are indicated. The photograph was taken in 1934 preceding the establishment of these water levels and during the period that the areas were being uniformly cropped to determine soil variability. The building at the rear houses the electric pumps that automatically control the water levels.

FIG. 2. (Lower left.) ONE OF THE COPPER CYLINDERS ENCLOSING PEAT IN SITU, WITH INLET AND OUTLET TUBES, TOGETHER WITH FLASKS FOR THE COLLECTION OF CARBON DIOXIDE, AND AN ARRANGEMENT TO CAUSE A FLOW OF AIR THROUGH THE SYSTEM

At the left is a tube extending down to an accumulation chamber for the collection of samples of soil air in the peat outside the cylinder.

FIG. 3. (Lower right.) THERMOGRAPH FOR RECORDING TEMPERATURES AT DIFFERENT DEPTHS IN PEAT

After the equipment was designed and installed to measure the amount of oxidation of a definite undisturbed mass of peat in place in the field, the problem remained of determining how much to aerate the peat so as to approximate normal conditions as closely as possible. Some preliminary trials were made, and it was decided to aspirate 3 liters of air through the cylinder in the field with the 12-inch water table and 4 and 6 liters, respectively, through the cylinders in the fields with 24- and 36-inch water table levels. As shown in table 1, considerably less carbon dioxide was removed in a second aspiration immediately following the first. The amounts recovered in a third period were about equal to those obtained in the second.

On the basis of the volumes of aspirational air recorded in table 1, the percentage concentration of carbon dioxide that accumulated in the cylinders was determined at the end of 4, 8, and 14 days (table 2). These percentages were compared with those in the soil atmosphere outside the cylinders collected in the manner described in a previous paper (5). The data indicate that the 4- and the 8-day intervals between collections were too short, as the concentration inside the cylinders in the field with the 36-inch level did not approach that outside the cylinders except when the interval was 14 days. In the field with the 12-inch water table, the concentration of carbon dioxide inside the cylinder was somewhat greater than that outside.

The results recorded in tables 1 and 2 indicated that the amounts of air recorded in table 1 should be drawn through the cylinders every 13 to 14 days. Approximately 26 collections of carbon dioxide per cylinder were obtained annually in this procedure, and the annual totals for duplicate cylinders on four of the fields are recorded in table 3 for a 5-year period. One cylinder only was used on the field with the 12-inch water table.

Before discussing the relation of subsidence or diminution of the surface levels of the peat in relation to the oxidation losses measured in these fields of differing water table levels it would be well to consider the data obtained in the resetting of the cylinders. In May, 1941, one of each of the duplicate cylinders was uncapped, removed, and reset. Table 4 records the pH, moisture content, ash, and nitrate and ammoniacal nitrogen of the peat inside and outside the cylinders. In the fields with the 24-inch and the 36-inch variable water tables, the pH of the peat inside the cylinders was about the same as in comparable samples outside; but in the fields with the 36-inch and the 24-36-inch water tables, it was higher inside. The moisture content of the peat inside the cylinders was somewhat higher than that outside in the 0-12-inch layers but showed no appreciable variations in the 13-18- and 13-24-inch layers. There were no consistent differences in the ash contents of samples inside and outside the cylinders. The accumulation of nitrate nitrogen was considerably higher inside two of the cylinders than outside, and these nitrates probably caused the lower pH values in the peat inside these two cylinders. It is not understood why nitrate accumulation was not higher in the other cylinders, since there was no leaching from rain in any of them. In general, the peat inside the cylinders was found to be similar in condition to that outside.

The cylinders that were removed were reset, and the carbon dioxide produced in the peat enclosed in them was measured for 1 year beginning May 30, 1941. The amounts of carbon dioxide thus obtained are recorded in table 5 together with those in the adjacent duplicate cylinders that had not been reset. The single cylinder on the field with the 12-inch water table was reset and the carbon dioxide from it is also recorded in table 5. In comparison with the original cylinders, the total carbon dioxide production for the year was slightly lower for one of the reset cylinders and somewhat higher for the other three. The production in the cylinder reset in the field with the 12-inch water table was about

TABLE 1

Carbon dioxide obtained from peat in field cylinders during successive periods of aspiration

PERIOD	WATER TABLE 12 INCHES; ASPIRA- TION PER PERIOD 3 LITERS	WATER TABLE 24 INCHES; ASPIRA- TION PER PERIOD 4 LITERS	WATER TABLE 36 INCHES; ASPIRA- TION PER PERIOD 6 LITERS	WATER TABLE 36 INCHES VARIABLE; ASPIRATION PER PERIOD 6 LITERS	WATER TABLE 24-36 INCHES; ASPIRATION PER PERIOD 6 LITERS
	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
1	27.8	481.0	769.1	724.4	834.8
2	13.6	115.2	275.1	99.6	333.4
3	12.2	96.9	248.0	51.5	271.0

TABLE 2

Concentrations of carbon dioxide in peat inside and outside cylinders for different periods between collections

DEPTH OF WATER TABLE	INTERVALS BETWEEN COLLECTIONS	CONCENTRATION OF CARBON DIOXIDE		
		In peat inside cylinders		In peat outside cylinders
		Before collection	After collection	
<i>inches</i>	<i>days</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
12	4	0.54	0.13	1.07
	14	2.87	0.29	0.97
36	4	3.50	0.80	8.52
	8	6.02	1.84	9.50
	14	8.41	3.38	9.79

the same as the yearly average for the 4-year period for that cylinder as recorded in table 3. A further inspection of table 3 will show that the differences in amounts of carbon dioxide obtained from duplicate cylinders for the year 1941 are no greater than some that occurred in previous years. From the comparisons of the peat inside and outside the cylinders (table 4) and of oxidation activity in newly set and undisturbed cylinders (table 5), it can be concluded that the peat inside the cylinders was in a condition similar to that outside except that nitrate accumulation tended to be higher inside. This was to be expected, since the peat inside the cylinders was not exposed to leaching from rain.

In addition to the subsidence measurements of these fields (3) a study was

made of the effect of water table level on the volume weight and ash of the peat. This was started in 1935 when the water table controls were established. Pre-

TABLE 3

Total annual collections of carbon dioxide from enclosed columns of peat in fields held at different water table levels

YEAR	WATER TABLE 12 INCHES	WATER TABLE 24 INCHES		WATER TABLE 36 INCHES		WATER TABLE 36 INCHES VARIABLE		WATER TABLE 24-36 INCHES	
		1	2	1	2	1	2	1	2
<i>Carbon dioxide collected, mgm.</i>									
1937	1,456.2	10,677.6	8,152.9	18,992.5	15,134.2	14,355.0	12,390.6	12,470.6	14,404.4
1938	979.1	12,526.1	10,017.0	15,468.9	17,173.1	13,554.0	11,478.5	15,498.1	15,139.6
1939	983.9	10,700.0	8,146.8	13,558.1	15,083.4	13,940.9	12,148.0	16,550.4	16,076.1
1940	981.8	10,025.1	8,781.7	13,168.5	14,192.3	14,926.9	11,859.4	15,371.4	16,152.6
1941	1,041.5	12,528.8	11,920.3	14,280.4	17,114.4	14,242.8	16,297.5	14,905.3	16,997.4
Average per year	1,088.5	11,291.5	9,403.7	15,093.7	15,739.4	14,203.8	12,834.8	14,959.2	15,754.1
Average per field	1,088.5		10,347.6		15,416.6		13,519.3		15,356.7
<i>Peat oxidized, mgm.</i>									
1937-1941	631.3		6,001.7		8,941.6		7,841.2		8,906.8

TABLE 4

Analysis of peat samples taken inside and outside cylinders, May 23, 1941

WATER TABLE LEVELS	SAMPLE DEPTH	INSIDE CYLINDERS					OUTSIDE CYLINDERS				
		pH	Dry matter	Ash	NO ₂ -N	NH ₂ -N	pH	Dry matter	Ash	NO ₂ -N	NH ₂ -N
<i>inches</i>	<i>inches</i>		<i>per cent</i>	<i>per cent</i>	<i>lbs./A.</i>	<i>lbs./A.</i>		<i>per cent</i>	<i>per cent</i>	<i>lbs./A.</i>	<i>lbs./A.</i>
24	0-12	4.95	27.08	11.80	350	9	5.05	30.59	10.36	20	15
	13-18	5.25	24.84	12.48	350	18	5.45	20.12	15.70	55	18
36	0-12	6.40	31.53	12.62	6	13	5.15	35.53	10.57	30	18
	13-24	6.40	22.72	13.29	0	15	5.70	24.17	12.03	40	18
36 (variable)	0-12	5.25	24.12	12.43	500	18	5.30	29.59	11.50	100	18
	13-24	5.25	23.68	12.17	500	13	5.85	22.93	10.54	150	25
24-36	0-12	6.25	20.66	11.29	10	18	5.30	30.43	11.09	5	15
	13-24	6.35	17.76	11.48	No trace	25	5.40	18.61	10.53	10	18

vicious to 1935 a 24-inch water table had been maintained in the area for 6 years but the land had not been plowed. The data of tables 3, 4, and 5 show that oxidation processes are active in a virgin area of that nature, causing the surface

layers of the peat to change from the original brown fibrous appearance to that of a blacker more plastic peat. When such an area is plowed, moled, and cultivated, the surface is compacted and the volume weight of the peat is increased, as evidenced in the soil-weight data for 1935 in table 6.

Table 7 shows the changes in volume weight and ash for a 6-year period as obtained from the data of table 6 for the fields of 12-, and 24-, and 36-inch water

TABLE 5

Amounts of carbon dioxide collected from peat in cylinders set in 1937 and in those reset in 1941

COLLECTION DATES	CARBON DIOXIDE COLLECTED								
	Water table 12 inches	Water table 24 inches		Water table 36 inches		Water table 36 inches variable		Water table 24-36 inches	
	Cylinder reset	Original cylinder	Cylinder reset	Original cylinder	Cylinder reset	Original cylinder	Cylinder reset	Original cylinder	Cylinder reset
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
1941									
May 30....	36.6	575.3	538.0	664.0	769.8	227.7	779.2	429.6	601.0
June 13....	25.7	611.2	431.6	695.2	736.6	655.9	702.0	558.3	618.6
25....	41.3	504.8	538.0	568.5	750.8	679.0	733.8	699.3	594.9
July 9....	36.6	533.3	566.5	686.4	732.5	672.2	744.0	681.7	645.8
23....	31.8	546.1	620.0	639.7	821.3	210.1	709.4	832.8	773.1
Aug. 11....	27.1	517.7	552.9	681.7	767.7	659.3	744.0	666.8	888.3
25....	39.3	563.8	582.7	489.2	940.5	689.8	827.3	603.7	849.7
Sept. 8....	31.2	532.6	611.9	652.5	858.5	727.1	723.0	613.9	790.8
23....	25.1	573.2	592.2	699.3	696.6	683.0	769.8	525.1	733.8
Oct. 14....	29.8	491.9	496.0	695.2	681.7	632.9	732.5	572.6	659.3
Nov. 3....	31.2	467.5	446.5	463.5	851.7	503.5	526.5	498.7	741.3
17....	12.2	542.8	530.6	632.9	763.0	699.3	855.1	611.2	716.9
Dec. 10....	73.2	587.5	498.0	355.1	814.5	636.3	562.4	918.8	826.7
23....	31.2	546.1	517.7	787.4	866.0	699.3	831.4	600.4	682.3
1942									
Jan. 9....	42.0	424.2	432.3	611.2	607.1	657.9	677.6	723.0	858.5
23....	17.6	502.8	393.0	520.4	656.6	627.5	688.4	568.5	721.6
Feb. 2....	21.0	433.0	391.7	425.5	523.1	496.7	456.0	660.7	667.4
16....	71.8	449.9	405.9	533.3	677.6	505.5	566.5	549.5	563.1
Mar. 13....	82.7	512.3	420.8	652.5	621.4	598.3	633.6	613.9	691.8
Apr. 3....	58.3	465.5	456.7	543.4	514.3	520.4	553.6	584.8	651.9
17....	75.2	467.5	446.5	463.5	641.7	503.5	526.5	498.7	741.3
May 3....	63.0	530.6	550.2	700.0	590.9	668.1	692.5	603.1	658.6
18....	67.1	473.0	425.5	673.5	571.2	681.0	633.6	681.7	757.6
June 5....	70.5	676.2	475.0	446.5	659.3	608.5	628.8	608.5	563.1
Totals.....	1,041.5	12,528.8	11,920.2	14,280.4	17,114.4	14,242.8	16,297.5	14,905.3	16,997.4

table levels. The field referred to as the 36-inch variable, is one in which the water table was periodically raised near to the surface and then dropped back to the 36-inch level. As shown in table 7 the volume weight of the top 6 inches increased slightly in three of the fields and decreased in the fourth. The ash content increased somewhat in all four fields, but like the volume weights, the changes were not consistent with the variation in water table levels. It is prob-

able that both volume weight and ash are slowly increasing in the surface layers of cultivated Everglades peat in which the water table is kept well below the sur-

TABLE 6

Volume weight and ash (oven-dry basis) of peat at different levels in water table plots in 1935, 1939, and 1941

WATER TABLE DEPTH	SOIL DEPTH	SOIL WEIGHT PER CUBIC FOOT			SOIL ASH		
		1935	1939	1941	1935	1939	1941
<i>inches</i>	<i>inches</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
12	1-6	16.2	15.6	18.2	10.15	12.74	12.69
	7-12	11.3	12.9	10.4	11.11	12.18	14.69
	13-18	12.0	10.9	11.9	18.65	15.27	18.43
	19-24	10.2	9.3	13.2	11.90	16.00	13.49
24	1-6	19.1	18.1	18.0	10.34	10.86	11.21
	7-12	14.4	15.5	11.5	11.16	11.20	12.66
	13-18	10.7	11.1	11.3	11.71	16.62	17.25
	19-24	11.6	9.7	8.2	17.72	14.37	10.38
36	1-6	17.4	18.6	17.6	9.79	10.66	12.29
	7-12	12.5	11.4	14.4	9.15	13.06	16.85
	13-18	11.8	11.7	8.8	19.70	16.67	11.38
	19-24	8.9	10.0	7.9	9.03	9.50	12.30
36 (variable)	1-6	18.0	19.2	20.4	9.53	10.37	12.11
	7-12	11.5	12.2	12.5	10.27	12.91	18.17
	13-18	11.8	10.9	8.5	15.49	19.72	11.17
	19-24	8.7	8.5	7.9	10.43	10.17	11.73

TABLE 7

Annual soil loss by oxidation and surface subsidence for 5 years and change in volume weight and in ash for an additional year for peat fields held at different water table levels

FACTORS DETERMINED	WATER TABLE LEVELS OF FIELDS			
	12 inches	24 inches	36 inches*	36 inches* variable
Soil loss per field cylinder annually in 5-year period				
.....gm.	0.63	6.01	8.94	7.80
Surface subsidence annually for 5-year period				
.....inches	0.55	1.46	1.80	1.66
Increase or decrease in weight per cubic foot of peat of top 6 inches for 6-year period.....lbs.	2.0	-1.1	0.2	2.4
Increase in ash of top 6 inches of peat for 6-year period.....per cent	2.54	0.87	2.50	2.58

* The water table levels in these fields averaged 4 inches less than 36 because of inability to keep the levels lower after the surface had subsided several inches.

face, but in the present instance the data were not based on enough replicated samples (duplicates only) to compensate for variations in samples and for the

errors of determination. The high and irregular ash of the 13-18-inch section is due to the plastic layer present in that zone and to some extent in the zones above and below.

In contrast to the irregular results for volume weight and ash, the average yearly subsidence and oxidation losses increased consistently with increase in water table level (table 7). These data show that under the conditions of the experiment an increase in depth of water table caused a greater increase in loss of peat by oxidation than of subsidence or diminution of the surface level. On the other hand, the amount of peat lost as measured by the oxidation that took place in the cylinders accounted for only a small part of the actual loss as indicated by the subsidence. Nor can the apparent disappearance of the peat be accounted for by compaction, since there was no appreciable increase in volume weight. The subsidence is proof that considerable loss occurs where the water table level is 24 to 36 inches below the surface, and it may be inferred that the rate of oxidation was less in the peat enclosed in the cylinders than in that not enclosed.

SUMMARY AND CONCLUSIONS

Equipment for the measurement of oxidation taking place in peat *in situ* was installed in fields of Everglades peat in which the water table levels were under constant control.

Several preliminary experiments were conducted to determine how much to aerate the columns of peat so as to keep the atmosphere in the enclosed peat similar to that of the surrounding masses. The amount of air drawn through the columns was made to vary with the particular water level of the field, since the height of the water table determined the length and hence the volume of the column.

Hydrothermographs were used to obtain a record of the effect of height of water table on the temperature of the peat at different levels below the surface, as well as to ascertain the temperature of the peat throughout the year, since temperature is known to affect greatly the rate of oxidation of peat.

By means of controlled aeration the carbon dioxide produced in the columns of peat was determined for a 5-year period. For a given column the amounts obtained did not vary much from year to year, nor were the variations excessive between duplicate columns. The rate of oxidation of the peat as shown by production of carbon dioxide depended strikingly upon the height of the water table. Thus the production in the columns located on the fields with the 24- and 36-inch tables was approximately nine and fourteen times greater, respectively, than that in columns in the field with a 12-inch water table. Oxidation of the peat in a field with a 24-36-inch water table that had never been plowed was equal to that of the peat in the cultivated field with a 36-inch water table.

The subsidence or diminution of the surface of the peat of these fields was in direct relation to the amount of oxidation as measured in the enclosed columns. The subsidence indicated a greater loss of peat than was accounted for by the carbon dioxide that was collected from the columns. Parallel studies of the changes in volume weight and ash of the peat of the cultivated fields showed that

the losses of peat could be attributed only slightly to compaction. It is probable that despite the attempt to keep the oxygen-carbon dioxide ratio of the peat in the columns similar to that without, the aeration of the columns was not sufficient to permit a fully normal rate of oxidation. The volume weight and ash studies indicate, however, that the subsidence of the peat was caused mostly by losses resulting from oxidation; and the experiments demonstrate that the amount of oxidation depends upon the height of the water table.

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A METHOD FOR DETERMINING THE TOTAL EXCHANGEABLE BASES OF SOILS

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In the determination of total exchangeable bases of soils, the bases are usually removed from the exchange complex by electrodialysis or by leaching with normal salt solutions or dilute acid solutions. The use of half-normal acetic acid as the leaching solution, recently proposed by Williams¹, has gained much favor in soil laboratories. Acetic acid is easily expelled by evaporation, and ignition of the residue converts the replaced bases into oxides and carbonates, the value of which can be accurately determined by titrating with a standard acid. The Williams method, however, is time-consuming and liable to error due to contamination. Whether the bases obtained by the Williams method of leaching represent the theoretical total exchangeable bases contained in the soil is another point requiring careful examination. The following experiments were carried out with these questions in mind.

SOME CRITICAL STUDIES ON THE WILLIAMS METHOD

Ten-gram soil samples were first leached with 400 cc. of 0.5 *N* acetic acid. Several additional 200-cc. aliquots of the leachate were then collected successively from the same soil samples. The total exchangeable bases were determined in the separate leachates. Williams' procedures were closely followed except that 0.1 *N* sulfuric acid was used in place of 0.1 *N* hydrochloric acid in the final titrations. The results of this experiment are recorded in table 1.

Soils 1 and 2 were taken from two successive horizons of a slightly podzolized yellow earth profile near Meitan. Soils 3, 4, and 5 were taken from three successive horizons of a rendzina soil profile near Meitan. Soils 6 and 7 were taken from two red earth profiles near Meitan. Soil 8 was taken from a vegetable garden in Tzun Yi.

The value obtained from the first 400-cc. leachate of each soil corresponds to the Williams value of total exchangeable bases. It will be seen that, in every case, by leaching the soil with more 0.5 *N* acetic acid than was prescribed by Williams, more exchangeable bases were removed from the soils. In several cases, even leaching the soil with 1200 cc. of 0.5 *N* acetic acid failed to effect complete removal of the total exchangeable bases. The difficulty of replacing all the exchangeable bases is especially obvious in the case of the garden soil.

EXPERIMENTS WITH THE SOXHLET APPARATUS

Since replacement of all the exchangeable bases by leaching with 0.5 *N* acetic acid was realized to be difficult, an attempt was made to effect more complete extraction by the Soxhlet extractor. The employment of this apparatus with a

¹ Williams, R. 1928 *Jour. Agr. Sci.* 18: 439-445.

slight modification was first reported by Salminen² in determining water-soluble electrolytes in soils. Heretofore, its use in studies of base-exchange problems has been unknown.

The apparatus used in the present study is that commonly employed for fat analysis. The extracting tube has a capacity of about 40 cc. and is connected with all-glass joints. In order to prevent dust particles or other impurities from entering the apparatus, a small U-shaped glass tube was joined to the upper end of the condenser by means of a rubber tube. The soil sample was loosely wrapped in an ashless filter paper and placed in the extracting tube. The extracting solution was poured into the extracting bottle. It was then heated to boiling. The boiling was regulated to have four to five back-flowings per hour. At the end of each hour, the solution in the whole extraction apparatus was emptied and analyzed for total exchangeable bases. Preliminary tests showed that during the extraction, the temperature of the extracting solution was main-

TABLE 1
Effectiveness of 0.5 N acetic acid in replacing exchangeable bases of soils

SOIL NUMBER	TOTAL BASES FOUND WHEN VOLUME OF LEACHATES AMOUNTED TO*				
	400 cc.	600 cc.	800 cc.	1000 cc.	1200 cc.
	m.e.	m.e.	m.e.	m.e.	m.e.
1	9.36	10.07	10.51	10.61	10.94
2	6.59	7.05	7.59	7.77	8.03
3	12.18	13.14	13.58	13.83	14.05
4	8.54	9.06	9.82	10.04	10.08
5	7.94	8.78	9.28	9.48	9.68
6	8.57	9.12	9.64	9.72	9.86
7	8.14	9.08	9.53	9.73	9.88
8	31.10	32.88	33.86	34.05	34.40

* Bases in m.e. per 100 gm. soil. Volume of leachates per 10-gm. soil sample.

tained at about 70° C. and never exceeded 75° C. The loss of acetic acid vapor through the condenser amounted to only a few milliequivalents in each case. The results of these extractions are presented in table 2.

It will be seen that by extracting the soil with dilute acetic acid in the Soxhlet apparatus, the quantity of exchangeable bases removed increased with the time of extraction. The greater the ratio between the soil and the extracting reagent, the steadier was the rate of increase. Thus, by extracting 10, 5, and 2.5 gm. of soil 1 with 100 cc. of 0.5 N acetic acid for 6 hours, the amounts of total exchangeable bases obtained were 7.51, 9.2, and 10.12 m.e. per 100 gm. of soil respectively. Decreasing the strength of the extracting reagent also decreased the amount of total exchangeable bases removed within a definite period. Thus, extracting 2.5 gm. of soil 1 with 100 cc. of 0.1 N acetic acid for 6 hours removed only 9.58 m.e. of exchangeable bases from 100 gm. of soil. Again, this state of affairs was especially noticeable in the case of the humus-rich garden soil. It is to be noted further that even extracting the soils for 9 hours did not exhaust all the ex-

² Salminen, A. 1928 *Proc. First Internatl. Cong. Soil Sci.* 2: 326-333.

changeable bases. Nevertheless, continuing the extraction after the 6-hour period gave less additional increase of exchangeable bases, indicating that the ultimate value was probably being approached.

TABLE 2

Total exchangeable bases in soils as determined by extraction with Soxhlet apparatus
Bases in m.e. per 100 gm. soil

SOIL NUMBER	METHOD OF EX- TRACTION*	TOTAL BASES FOUND ON EXTRACTION IN SOXHLET APPARATUS								
		1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	9 hrs.
1	A	2.65	5.10	6.12	6.77	7.26	7.51	7.61	7.74
	B	5.93	6.74	7.03	8.86	9.20	9.82	10.24
	C	4.44	6.89	7.89	8.92	9.61	10.12	10.57	10.69
	D	7.85	9.15	9.58	9.94	10.22
2	A	1.21	2.60	3.99	5.19	5.69	6.23
	B	4.32	5.53	5.74	6.26	6.86	7.41	7.89
	C	3.97	5.85	6.28	6.69	7.34	8.30	8.76	8.98
	D	5.82	7.16	7.85	8.48
3	A	4.59	7.43	9.88	11.88	12.58	13.30	13.72
	B	9.48	10.48	11.88	12.68	13.30	13.90
	C	10.72	13.28	13.68	14.08	14.08	14.08
	D	9.68	11.00	12.00	12.84	13.84	14.24
4	A	3.32	5.52	7.43	8.63	9.10	9.51
	B	6.40	7.65	8.43	8.98	9.23	10.02	10.61	10.88
	C	5.94	7.55	8.57	9.38	10.02	10.53	10.76
	D	7.88	9.12	9.54	9.68
5	A	1.56	3.12	4.64	5.51	6.35	6.95
	B	5.20	6.44	7.74	8.72	9.26	9.76	10.60	10.90
	C	3.20	7.66	8.38	9.22	9.76	9.90	10.22
	D	5.00	6.00	7.80	8.68	9.16	9.76
6	A	2.15	4.21	5.92	6.79	7.69	8.52
	B	5.33	6.22	7.85	8.41	8.88	9.12
	C	4.17	6.28	7.80	8.74	9.42	9.93	10.55
	D	7.52	8.33	9.23	9.56
7	A	1.15	2.94	4.38	5.19	6.11	7.03
	B	3.86	5.22	6.47	7.35	8.14	8.76	9.23
	C	4.02	5.77	7.08	8.26	9.10	9.57	10.10
	D	5.43	7.38	8.34	8.82
8	A	4.30	9.02	14.26	17.03	19.53	21.90	23.70	26.17	26.89
	B	18.66	24.24	26.60	29.30	32.10	33.46	35.20	36.05
	C	13.40	23.40	30.60	34.00	36.48	37.20	37.42
	D	12.80	18.88	22.68	26.88	29.76	31.56	33.08	34.28

* A, B, C = 10, 5, and 2.5 gm. soil extracted with 100 cc. 0.5 N acetic acid; D = 2.5 gm. soil extracted with 0.1 N acetic acid.

The Soxhlet extraction method is simple of manipulation. The extraction takes place in an enclosed system, and contaminations from outside sources are impossible. The quantity of acetic acid used in the extraction is less than that required by the Williams method of leaching; consequently the time required for evaporation is much shorter, and chances of contamination are further minimized. The only disadvantage is the prolonged extraction necessary for a complete removal of the exchangeable bases. This difficulty could be easily overcome, however, by carrying out the extraction overnight in an electrically heated Soxhlet apparatus. The 0.1 *N* acetic acid seems to be preferable to the 0.5 *N*, as it has less solvent effect on the exchangeable complex. This is evidenced by the fact that yellow specks remained after ignition of the dried residues from the 0.5 *N* acetic acid extraction, whereas the residue from the 0.1 *N* acetic acid extraction gave no such specks and dissolved completely in the standard sulfuric acid.

SUMMARY

A critical study of the Williams method of determining total exchangeable bases of soils showed that the leaching of 10 gm. of soil with 400 cc. of 0.5 *N* acetic acid failed to replace all the exchangeable bases. The procedure is tedious, time-consuming, and liable to errors due to contamination. A simple and more reliable method of extracting the soil in a Soxhlet apparatus is proposed.

PHYSICOCHEMICAL PROPERTIES OF FERROALUMINOSILCATES AS ALLIED TO SOILS

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The soil, in a broad sense, consists of the mineral framework and of salts, organic matter, and water in varying quantities. The mineral material is by far the most important from the point of view of soil genesis. It consists of mineral fragments of the parent rock in various stages of disintegration brought about by weathering agencies such as frost and snow, wind and rain.

Clay may be regarded as a weak electrolyte, as it is built up of acidic and basic radicals. In fact, a silicate clay may, for all practical purposes, be considered as a salt made up of a great number of positive radicals and of a very complex iron and aluminum silicate acid radical which is insoluble, stable, and highly hydrated. Clay can enter into double decomposition with other salts, the cations being exchanged in equivalent quantities. The senior author, in a series of papers, has shown that a clay suspension behaves like a weak electrolyte in a variety of ways. For example, its cations undergo reactions involving precipitations and double decompositions that are no different from similar reactions of soluble salts (10). The separation of its cations and anions by electric current (electrodialysis) is no different fundamentally from ordinary electrolysis of soluble salts, and its polarographic current voltage curves are no different from similar curves for soluble salts (11).

The rapidity with which the exchange of the cation takes place when clay is brought into contact with a salt solution suggests that the clay cations are all on the surface of the particles. This is also indicated by the fact that clay suspended in water develops an electronegative charge, as would be expected if some of the cations ionize on the surface. With the increase in surface exposed by particles, increase in base exchange and other physicochemical properties of soil is to be expected.

The exact constitution of the complex anion (the "acidoid" to retain Michaelis' term), the core of the particle, is still obscure, and very little is known regarding the form in which the hydrous oxides of silicon, iron, and aluminum exist in soil. Clay is stable as long as it is fairly well saturated with the bases, but its stability decreases as some of the bases are removed, and when the pH falls below a certain value it tends to give up iron and aluminum oxides. From the literature dealing with this subject it appears that most investigators assume the existence of combinations in the form of hydrous silicates. Although some look upon these combinations as definite compounds of the nature of kaolinite silicates of higher molecular ratio, others look upon them as adsorption compounds of uncertain composition formed by the mutual precipitation of the colloidal oxides of opposite sign of charge (2, 21, 23).

Bradfield (3) prepared an artificial mixture of the colloidal oxides (SiO_2 , Al_2O_3 , Fe_2O_3 , etc.) in the proportion in which he found them to be present in a typical sample of clay and compared the properties of the mixture with those of the clay. The properties were found to be entirely different, inasmuch as the natural colloid (clay) was electronegative, whereas the mixture was electropositive. Furthermore, the mixture had much stronger buffer action than the natural colloid. Bradfield, therefore, concluded that the natural colloid is not a mixture of colloidal oxides. He also argued that since natural clay is flocculated most easily in an acid medium, it cannot contain much free silica. It thus seems highly probable that the clay acidoid is a complex aluminosilicate. After a detailed study of various samples, Bradfield gave the molecular ratio of alumina and silica as 1:3 and assigned to the acidoid a dissociation constant of the same order as carbonic acid (4). Puri and Asghar (12) calculated values of dissociation constants of free acidoids from which the bases had been removed altogether, and found some of them to be as strong as acetic acid, though the majority were found to be only slightly weaker than uric acid.

There is little doubt that in clay we are dealing with ferroaluminosilicates and that the free acidoid (SiO_2) valencies uncombined with the ampholytoid (Fe_2O_3 , Al_2O_3) valencies constitute the seat of cation exchange. These acidic properties are intensified in the presence of humic acid in natural soils. We are still not in a position, however, to demonstrate an exact parallelism between the properties of ferroaluminosilicates and soil colloids. Raychaudhuri (20) recently made a useful contribution to the subject by studying the electrokinetic and the cation and anion exchange properties of synthetic aluminosilicates of varying $\text{SiO}_2/\text{R}_2\text{O}_3$ ratios and comparing them with similar properties of natural clays like kaolin and limonite. The synthetic aluminosilicates were prepared by mixing silicic acid and aluminum hydroxide sols in varying proportions. No other serious attempt seems to have been made to study exhaustively the various physicochemical properties of these compounds and to show that *the simplest iron and aluminum silicates prepared in the laboratory do exhibit all the essential properties characteristic of the clay complex in the soil.*

In the investigations described in the present paper, some of the characteristic physicochemical properties common to soil colloids were studied in several mixtures of ferroaluminosilicates of varying composition. The paper shows how closely the mixtures, subject to the limitations inherent in a laboratory product, resemble the soil colloids in essential respects.

EXPERIMENTAL

Preparation and preliminary treatment of ferroaluminosilicates

Mixtures of varying silica, alumina, and ferric oxide ratios were prepared by adding solutions of different concentrations of ferric and aluminum silicate. The precipitates were washed over Büchner funnels with 0.05 N HCl to remove unreacted sodium silicate and exchangeable cations, if any, then with distilled water until free from chloride ions, and finally with alcohol. The precipitates

were then dried. The chemical composition of the mixtures as determined by the usual methods of analysis is given in table 1.

The following properties of the mixtures were studied: mechanical analysis, moisture absorption at various humidities, catalytic activity of acidoids, titration curves, and ammonia absorption.

Mechanical analysis

The determination of clay and ultraclay particles is of particular importance in the mechanical analysis of soils, as these particles alone are supposed to be responsible for the base-exchange properties and the colloidal behavior of soils.

As the mineral particles of soils exist largely in the form of aggregates, the constituent particles of which are held together by cementing colloidal materials, a sample, before being subjected to mechanical analysis, must be dispersed, i.e., the aggregates must be resolved into ultimate primary units. Several methods,

TABLE 1
*Chemical analysis of ferroaluminosilicate mixtures**

MIXTURE NUMBER	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	SiO ₂ Fe ₂ O ₃ + Al ₂ O ₃
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
1	19.3	0.00	55.7	2.89
2	13.7	3.2	55.5	3.28
3	11.3	6.3	57.2	3.25
4	9.7	8.3	58.4	3.25
5	9.5	8.7	59.8	3.28
6	9.4	9.6	62.5	3.29
7	5.4	11.3	66.3	3.97
8	3.3	13.9	71.2	4.14
9	0.0	15.4	76.0	4.94

* The difference between 100 per cent and the total constituents of each mixture is due to water of hydration.

both mechanical and chemical, for dispersing soils are known. In order to find a suitable method for dispersing ferroaluminosilicates, the following methods, often used in soil analyses, were tried on one of the mixtures:

1. Shaking the suspension for 24 hours in a mechanical shaker with enough NaOH to raise the pH value to 10.8 (14).
2. Wet-grinding of the mixture with a rubber pestle and subsequent shaking for 24 hours in a mechanical shaker (8).
3. Same as method 2 but enough NaOH added to raise the pH value to 10.8 before shaking.
4. Shaking for 24 hours with coarse sand (1 mm. diameter) to the amount of fivefold the weight of the sample (19).
5. Same as method 4 but enough NaOH added to bring the pH value to 10.8 before shaking.

The results of mechanical analysis, determined by means of the chainohydrometer (16) are given in table 2. It will be seen that methods 1, 3, and 5 are about

equally efficient, whereas the purely mechanical methods 2 and 4 do not produce maximum dispersion but give a state of aggregation which is the same in both cases.

It has been shown (17) that various methods of soil dispersion which are equally efficient if reckoned on the basis of conventional clay (0.002 mm.) may give entirely different size distributions in the ultraclay region. In order, therefore, to determine how these three methods compare so far as dispersion of ultraclay is concerned, the suspensions obtained by methods 1, 3, and 5 were subjected to ultramechanical analysis by the micropipette technique (18). The results,

TABLE 2

Mechanical analysis of ferroaluminosilicate mixture 4 dispersed by various methods

METHOD OF DISPERSION*	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES				
	0.06 mm.	0.02 mm.	0.01 mm.	0.005 mm.	0.002 mm.
1	78.4	43.9	28.2	17.2	14.15
2	83.9	44.05	7.6	6.8	2.1
3	73.1	45.1	31.1	17.9	14.7
4	85.5	44.0	8.0	7.1	1.75
5	76.0	44.0	32.7	27.6	16.90

* See text for description of methods.

TABLE 3

Ultramechanical analysis of mixture 4 dispersed by various methods

METHOD OF DISPERSION*	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES		
	0.001 mm.	0.00063 mm.	0.00025 mm.
1	0.0	0.0	0.0
2	1.9	0.8	0.0
3	4.4	3.6	2.1

* See text for description of methods.

given in table 3, show clearly that Method 3 is the most efficient. The total dispersion in the ultraclay region, however, is still very low.

For silicate mixtures, thus, we find that the chemical method of dispersion is successful only when some preliminary mechanical treatment such as grinding with a rubber pestle has been given. Soils, on the other hand, disperse to the maximum degree when they are merely left in contact with water containing enough NaOH to raise their pH values to 10.8. No subsequent shaking and no preliminary mechanical treatment are needed (14). This is shown by the results in table 4, which were obtained by dispersing an acid-treated soil by shaking with NaOH at pH 10.8 with and without the preliminary grinding with a rubber pestle. The two sets of values for various ultraclay fractions are almost identical.

This difference in the two cases is probably due to the fact that the mixtures of the silicates prepared in the laboratory have not undergone natural disintegration and weathering as have the soils. In fact, grinding with a rubber pestle as

a preliminary mechanical treatment may not be sufficiently drastic to put these mixtures on the same footing as natural soil.

A more drastic mechanical treatment, grinding in a colloid mill, was also tried on the mixtures of silicates. The colloid mill was a mechanically driven agate pestle and mortar which gave efficient and thorough grinding of the material. The time of grinding required for the maximum effect was determined by taking a 5-gm. portion of a mixture, working it into a thin paste with water, and subjecting it to the action of the colloid mill for various intervals of time. The ground material, in each case, was transferred to a separate bottle and shaken with the requisite amount of alkali for 24 hours as usual. The results are given

TABLE 4

Effect of preliminary grinding on ultramechanical analysis of soil P. C. 13

TREATMENT	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES					
	0.002 mm.	0.001 mm.	0.00025 mm.	0.0001 mm.	0.000063 mm.	0.00004 mm.
No preliminary mechanical treatment.....	59.2	58.6	50.2	45.8	36.8	26.4
Preliminary treatment with rubber pestle.....	59.7	57.8	50.6	46.4	36.2	25.7

TABLE 5

Effect of time of grinding in a colloid mill upon dispersion of silicate mixture 4

TIME OF GRINDING	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES						
	0.01 mm.	0.005 mm.	0.002 mm.	0.001 mm.	0.00025 mm.	0.0001 mm.	0.000063 mm.
<i>minutes</i>							
15	61.4	45.2	27.3	20.3	8.1	5.1	1.9
30	67.3	51.4	33.6	23.5	9.3	7.2	3.2
60	77.9	66.5	49.9	32.8	12.9	10.3	4.1
120	76.5	67.2	48.5	31.7	12.1	9.8	3.5

in table 5 and show that 1 hour of grinding is required to produce the maximum effect. Further grinding does not increase the dispersion.

The various mixtures were then dispersed by rubbing with a rubber pestle and by grinding in a colloid mill for 1 hour as mechanical treatments preliminary to chemical dispersion (shaking with NaOH at pH 10.8) and were subjected to complete mechanical and ultramechanical analyses. The results are given in tables 6 and 7.

Another set of each of these mixtures was subjected to grinding in a colloid mill for 1 hour and then air-dried. It was redispersed by grinding with a rubber pestle followed by shaking with NaOH for 24 hours. The results of the mechanical analysis are included in table 7.

Comparison of the results in table 6 and those in the upper rows of the different mixtures shows that preliminary grinding in a colloid mill produces far more

TABLE 6

Mechanical analysis of silicates dispersed by grinding with a rubber pestle and shaking with alkali at pH 10.8

MIXTURE NUMBER	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES								
	0.06 mm.	0.02 mm.	0.01 mm.	0.005 mm.	0.002 mm.	0.001 mm.	0.00063 mm.	0.00025 mm.	0.0001 mm.
1	75.2	48.8	24.5	19.9	16.5	5.5	3.9	2.3	1.5
2	75.9	37.2	23.5	20.7	16.3	4.4	3.6	2.0	1.3
3	75.9	37.2	28.7	17.3	13.5	4.9	3.7	2.3	1.7
4	74.1	44.9	41.6	17.9	14.3	4.7	3.6	2.1	1.7
5	74.5	44.3	39.9	16.7	12.3	3.7	2.3	1.5	0.7
6	78.7	49.8	30.6	16.9	12.1	2.5	1.5	0.8	0.6
7	77.9	50.8	32.3	15.3	10.5	2.3	1.0	0.6	0.2
8	79.3	51.2	33.6	12.7	7.8	2.1	1.2	0.8	0.5
9	83.4	53.6	33.9	11.5	8.4	2.3	1.0	0.8	0.5

TABLE 7

*Mechanical analysis of silicates dispersed by grinding in a colloid mill and subsequent shaking with NaOH**

MIXTURE NUMBER	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES									
	0.06 mm.	0.02 mm.	0.01 mm.	0.005 mm.	0.002 mm.	0.001 mm.	0.00063 mm.	0.00025 mm.	0.0001 mm.	0.000063 mm.
1	82.1	75.3	72.3	71.1	53.4	38.4	18.3	12.3	5.6
	79.3	62.5	49.2	46.6	33.7	13.2	8.5	5.9	4.9	2.1
2	82.9	77.4	72.9	71.5	51.3	36.5	23.5	16.2	9.7	4.2
	80.4	65.3	51.3	43.3	32.2	13.1	7.6	5.4	3.9	1.5
3	85.3	78.0	75.9	70.8	48.7	34.1	21.2	13.5	9.3	4.1
	81.9	65.9	53.5	42.9	31.9	13.1	6.3	4.9	3.8	1.2
4	85.9	79.3	78.3	67.3	49.1	32.1	20.9	12.1	9.5	3.6
	83.5	67.7	53.3	42.1	30.1	11.4	6.3	4.5	2.9	1.6
5	87.3	78.4	78.3	46.2	30.1	19.5	10.6	8.6	3.6
	84.3	67.9	55.9	40.3	30.4	8.5	4.2	3.3	2.7	0.7
6	87.4	84.5	76.6	66.9	43.0	24.1	15.3	10.3	8.2	2.9
	85.9	71.3	58.6	39.7	28.1	8.3	3.3	3.2	2.1	0.00
7	93.6	83.9	79.6	65.3	42.9	22.2	17.6	9.6	8.1	2.3
	87.6	72.3	59.6	38.2	26.2	8.4	2.2	2.9	2.1	0.5
8	97.4	85.6	80.3	65.4	39.9	19.3	16.4	9.4	6.7	2.2
	88.5	73.6	61.9	39.1	24.3	6.9	2.4	2.8	1.9	0.6
9	98.1	85.9	83.9	54.3	38.5	19.5	16.2	9.2	5.3	1.9
	88.6	73.9	62.3	37.2	20.1	6.2	2.1	2.1	1.8	0.4

* The values in the lower row for each mixture were obtained by air-drying the mill-ground material and then dispersing it by means of the rubber pestle treatment before shaking with alkali.

clay than does rubbing with a rubber pestle. Furthermore, the figures in table 7 for mixtures subjected to mill-grinding as the only preliminary mechanical treatment differ considerably from the figures in the same table for mixtures subjected also to air-drying and regrinding with a rubber pestle. This is evidently due to the fact that grinding breaks down the aggregates into smaller particles which remain as such in the wet state but recombine on drying to form crumbs again.

It will be seen from table 7 that the first four mixtures have approximately the same mechanical composition and the same amount of clay and ultraclay fractions. The succeeding mixtures contain decreasing amounts of clay as well as of ultraclay particles. The differences, however, are probably only apparent. As shown in table 1, the mixtures are numbered in the order of decreasing amounts of iron and increasing amounts of aluminum. It appears that when the aluminum content of a mixture increases beyond a certain limit, partial dissolution of aluminum silicate takes place in the alkaline solution. This causes partial coagulation of the suspension, which is reflected in low values of clay and ultraclay fractions. As the aluminum content of a mixture increases further, the dissolution and therefore the coagulation effects become more and more pronounced, resulting in further lowering of the values of clay and ultraclay fractions. As iron silicate resists the dissolution action of alkali, no such effect is noticed in mixtures rich in iron. Evidence on this point has been brought forth in these laboratories.¹

In soils no such dissolution of aluminum takes place as long as the quantity of alkali added is not appreciably large and the pH does not rise much beyond 11. In fact, soils rich in aluminum yield fairly stable suspensions. This may be attributed to the fact that natural soil colloids contain complex (compound) ferroaluminosilicates, whereas laboratory silicates are simple mixtures of iron and aluminum silicates. Furthermore, ageing is likely to make soils comparatively more resistant to the action of alkali.

Soils are known to be completely dispersed at pH 10.8 (14). At lower pH values, the dispersion is small, and any rise in pH value gradually causes increased dispersion.

In order to determine the dispersion of silicates at various pH values, four mixtures were given preliminary treatment with a rubber pestle, and their 1 per cent suspensions were prepared. The clay content (<0.002 mm.) was determined by means of the chainohydrometer in each case on the gradual addition of increasing amounts of NaOH. After each addition of NaOH the suspensions were put aside for 48 hours (with occasional shaking by hand) before the clay percentage was determined. The pH values of the suspensions were also noted at the same time by means of the glass electrode. The results are plotted in figure 1. Dispersion of an acid-treated soil at different pH values determined in the same manner as in the case of the silicate mixtures is also shown in figure 1. The similarity of all the curves is very striking. Thus these mixtures behave like soils as far as dispersion is concerned. Just as dispersion in soils increases gradually with a rise in pH value and reaches a maximum at pH 10.8 to 11.0,

¹ Dhawan, B. Solubility of sparingly soluble silicates of Fe and Al in buffer solutions of acids and alkalies. (Unpublished master's thesis, 1940.)

so dispersion in mixtures continues to increase with the pH value, to about 10, at which point the increase becomes more abrupt and is continued until the maximum value of clay is attained at about pH 11.

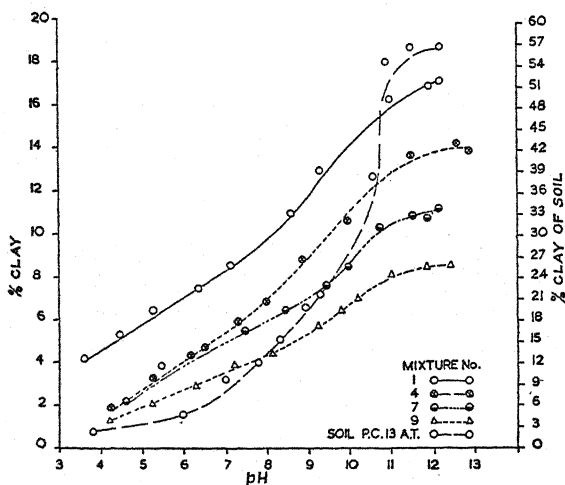


FIG. 1. DISPERSION OF FERROALUMINOSILICATES (AFTER GRINDING WITH A RUBBER PESTLE) AT DIFFERENT pH VALUES

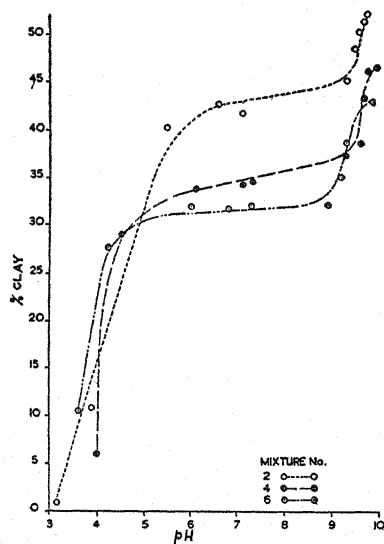


FIG. 2. DISPERSION OF FERROALUMINOSILICATES (AFTER GRINDING IN COLLOID MILL) AT DIFFERENT pH VALUES

The dispersion of silicates at different pH values after grinding in a colloid mill is shown in figure 2. The curves are steeper and the maximum values for clay content are obtained at much lower pH values than when the grinding is

done with a rubber pestle. This shows that when the chemical method of dispersion is aided by such drastic mechanical methods as grinding in a colloid mill for 1 hour, the maximum dispersion is brought about much sooner. In other words, the effects of chemical and mechanical dispersion are additive. But it will be readily seen that grinding in a colloid mill alone, however drastic this treatment may be, cannot produce any marked dispersion (fig. 2). Addition of alkali is essential for dispersion.

Moisture absorption at different humidities

The absorption of moisture from atmospheres saturated with water vapors has been extensively used for characterizing soils. The difficulty of such measurements and the uncertainties involved have been discussed by Puri (6). The absorption of moisture from partly saturated atmospheres is more definite, and

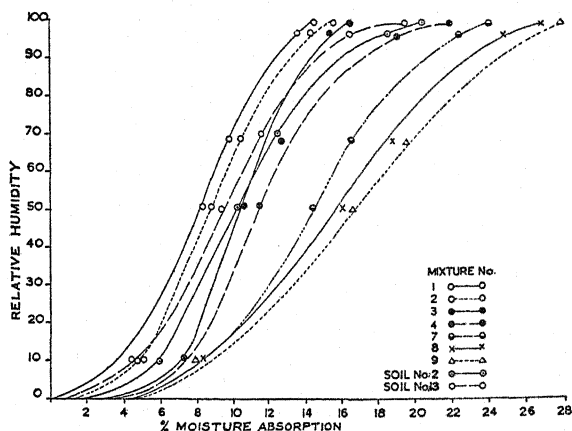


FIG. 3. RELATION BETWEEN MOISTURE CONTENT AND RELATIVE HUMIDITY IN FERRO-ALUMINOSILICATES AND SOILS

precise measurements can be made at any relative humidity by the use of mixtures of sulfuric acid and water in different proportions (7).

In order to determine moisture absorption at various humidities, the mixtures were dried over sulfuric acid and then kept in a vacuum desiccator containing H_2SO_4 -water mixtures corresponding to 10, 50, 68, 96, and 99 per cent relative humidities. The increase in weight was determined after 5 days and the percentage moisture absorption calculated therefrom. The values are plotted in figure 3.

In figure 3 are included moisture absorption curves of two soils as well. The similarity in the shapes of the moisture absorption curves for the silicates and the soils is remarkable. The hygroscopicity will be further seen to increase with an increase in silica/sesquioxide ratio as well as with an increase in alumina content.

The amount of moisture absorbed between the 10 and 70 per cent interval of humidity has been shown by Puri (9) to be significantly correlated with the clay content of soils by an empirical formula:

$$\text{Clay} = 8.41 H + 2.8$$

where H is hygroscopicity (moisture absorption between 10 and 70 per cent humidities). By means of this formula, the clay contents were calculated for all the mixtures and soils included in figure 3. The values are given in table 8. The values of clay (<0.002 mm. as well as <0.001 mm.) for the mixtures and the soils as determined by mechanical analysis are also included in the table.

The method of dispersion employed for silicates was grinding in a colloid mill followed by shaking with NaOH for 24 hours at pH 10.8. It will be seen that whereas the agreement between the determined and the calculated values for soils is best when the percentages of particles <0.002 mm. are not taken into consideration, the agreement for the first four silicates is valid only when the percentages of particles <0.002 mm. are taken into account. Mixtures 7 and 8 give lower values than the calculated ones. This, as already mentioned, is due to the fact that the results of mechanical analysis of the mixtures with high aluminum contents are masked by the partial dissolution of aluminum silicate

TABLE 8

Clay content as calculated by moisture absorption between 10 and 70 per cent humidity in comparison with that determined by mechanical analysis

MIXTURE OR SOIL NUMBER	CLAY DETERMINED		CLAY CALCULATED
	0.002 mm.	0.001 mm.	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Mixture 1	53.4	38.4	49.5
2	51.3	36.5	51.5
3	48.7	34.1	51.1
4	49.1	32.1	50.7
7	42.9	22.2	82.9
8	39.9	19.3	91.8
Soil 2	59.1	53.4	51.1
13	58.2	54.0	53.2

in alkaline solutions. This results in the partial coagulation of the suspension. For this reason the values for clay content as calculated from the moisture absorption curves may be more reliable. Furthermore, the high values of clay as obtained from moisture absorption curves of silicates with increasing amounts of aluminum would explain the increased activity of acidoid in them as shown in the following section.

Titration Curves

Titration curves of soils were first determined by Sharp and Hoagland (22). Bradfield (3) determined titration curves of clays separated from soils and pointed out a close analogy between soil acidoids and true acids on account of the general similarity of the curves. The clay suspensions studied by him were not electro-dialyzed or acid-treated, and consequently a portion of the acidoid was already neutralized, and titration curves were thus incomplete. In later studies Bradfield (4) used electro-dialyzed clay. Anderson and Byers (1) studied the neutrali-

zation curves of clays and recommended shaking the suspension with alkalior acid, as the case may be, for 36 to 48 hours in order to bring about equilibrium before determining the pH value.

Puri and Asghar (12) studied the titration curves of a number of acid-treated soils and showed that acidoids closely resemble weak dibasic acids. The point of inflection in titration curves was found to occur approximately 4 pH units above the initial pH value of the acidoid. This was taken to correspond to the neutralization of the first hydrogen (soil acidoid being regarded as dibasic), as the titration is not completed at the first point of inflection.

The titration curves of the silicates were determined by using Puri's technique. Increasing amounts of standard alkali (NaOH) were added to 1-gm. portions of the mixtures, and volume was made to 10 cc. in each case. The suspensions were shaken continuously for 48 hours in a mechanical shaker, after which the pH values were determined with the glass electrode.

The titration curves so obtained are plotted in figure 4. It will be seen that as the percentage of silica decreases (table 1), the titration curve shifts upward; in other words, the mixture behaves as a weaker acidoid. The relative amounts of iron and aluminum hydroxides in the mixtures would also influence the degree of acidity of the mixture, because ferric hydroxide is a stronger base than aluminum hydroxide, and, therefore, on combination with silica it would leave a weaker acid residue than the aluminum hydroxide.

The titration curves of a few soils are given in figure 5. Although the natural soils are found to possess comparatively lower buffer capacities, the striking similarity of the soil titration curves to the silicate titration curves is well brought out and should leave no doubt that in soils we are dealing with similar compounds. The variations in soils, therefore, can be satisfactorily accounted for by variations in the silica/sesquioxides ratios as well as by the nature and the amount of the sesquioxide.

As with soils, the point of inflection in the titration curves of silicates occurs at about 4 pH units higher than the initial pH value, and therefore, on the analogy of soils, this point should correspond to half neutralization of the total acidoid in the ferroaluminosilicate mixtures. The amount of alkali required for such half neutralization is usually denoted by $T/2$ and corresponds to the base-exchange capacity of the acidoid (12). The $T/2$ values for the various mixtures of silicates in terms of milliequivalents per 100 gm. of mixtures as calculated from their titration curves (fig. 4) are given in table 9. It will be seen from table 1 that the silica/sesquioxide ratio as well as the nature of the sesquioxide determines the base-exchange capacity of the acidoid to a large degree. Further, it will be seen that the maximum exchange capacity occurs at a certain $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio, beyond which it begins to fall. This is in accordance with the observations of Mattson (5) and Raychaudhuri (20).

Puri (12) has calculated dissociation constants of soil acidoids from their titration curves by applying the usual mass law equation of weak acids,

$$\text{pH} = \text{pK} + \log \text{salt/acid.}$$

When the acid is half neutralized, i.e., the ratio salt/acid is unity, $\text{pH} = \text{pK}$, where pK is the logarithm of the reciprocal of its dissociation constant, just as pH is the logarithm of the reciprocal of the hydrogen-ion concentration. By applying the same principle, the pK values of the silicate mixtures were calculated from their titration curves (fig. 4). These values, given in table 9, are of

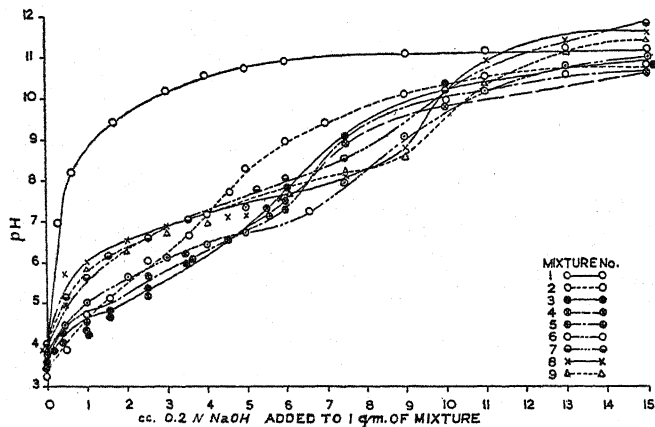


FIG. 4. TITRATION CURVES OF FERROALUMINOSILICATES

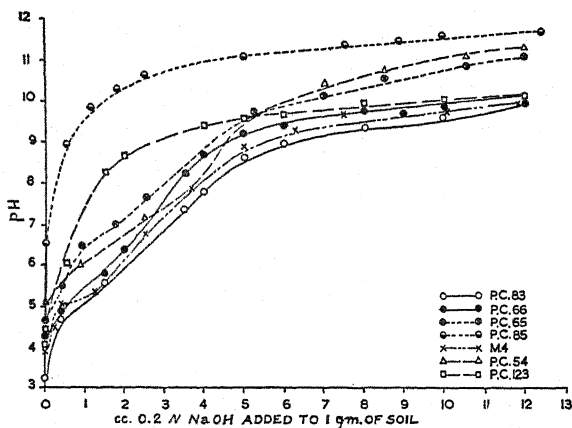


FIG. 5. TITRATION CURVES OF SOILS

the same order of magnitude as those generally found in soils. The artificial silicates are thus similar to soils in this respect.

Activity of acidoid in silicate mixtures

The $T/2$ values given in table 9 represent what may be described as the quantity factor of the acidoid, which has been shown to increase with the increase in silica and alumina contents. The intensity or the activity of the acidoid is usually expressed by the pH value. Another method well known in

physical chemistry for comparing the activity coefficient of acids is by measuring the catalytic activity of the H ions furnished by the acids in bringing about the hydrolysis of esters or the inversion of cane sugar. Puri and Dua (15) compared the activity coefficients of the various soil acidoids in this way and found a significant correlation between the pH value and the activity coefficient.

The hydrolysis of ethyl acetate was studied with the mixtures of ferroaluminosilicates. The procedure adopted was to mix 5-gm. portions of the various mixtures with 25 cc. of 5 per cent ethyl acetate solution. The suspensions were kept at 50° C. for 4 hours, during which they were shaken by hand at frequent intervals. After this they were cooled and filtered and an aliquot was titrated against standard alkali. The quantity of acetic acid produced is given in table 10. The values are seen to increase in the order of increasing amounts of silica and alumina in the mixtures.

The soil acidoids on coming into contact with neutral salts, such as KCl, bring into solution true acids, together with some aluminum and iron, which also be-

TABLE 9

T/2 Values, ammonia absorption, and pK values of various silicates

MIXTURE NUMBER	T/2 PER 100 GM. OF SILICATE	pK	NH ₃ RETAINED PER 100 GM. OF SILICATE
	<i>m.e.</i>		<i>m.e.</i>
1	16.0	5.85	20.0
2	83.0	5.62	77.0
3	113.0	5.60	113.0
4	110.0	5.85	127.5
5	125.0	5.92	135.0
6	140.0	6.30	142.5
7	145.0	6.95	145.0
8	155.0	7.12	159.5
9	142.0	7.10	153.0

have like acids, though they can be distinguished from the true acids by the use of methyl orange as the indicator during titration with alkali. It was of interest to determine the relation, if any, between the hydrolyzing power of the mixtures and the acid set free on shaking with KCl. For this purpose, 5-gm. portions of the mixtures were shaken with 100 cc. of N KCl solution for 2 hours and filtered. An aliquot of the filtrate was titrated with standard alkali, phenolphthalein being used as the indicator. Another aliquot was titrated with the same alkali, methyl orange being used as the indicator. The values obtained are given in table 10. It will be seen that the values of acid displaced by KCl increase in the same order as the values of acetic acid produced by hydrolysis of ethyl acetate. In this respect also, the synthetic mixtures of the silicates resemble natural soils.

Ammonia absorption

The following procedure was adopted in determining ammonia absorption by the mixtures of silicates:

A 5-gm. portion was kept in contact with excess ammonia for 48 hours. The suspension was then boiled to half its volume, and the ammonia retained by the mixture was determined by distilling with excess of lime.

The amounts of ammonia taken up by 100 gm. of the various mixtures are given in table 9 along with the $T/2$ values. It will be seen that the amount of

TABLE 10
Acid produced by ferroaluminosilicates on hydrolysis of esters and on shaking with KCl

MIXTURE NUMBER	CH ₃ COOH PRODUCED PER 100 GM. OF SILICATE	HCl PRODUCED PER 100 GM. OF SILICATE	
		Phenolphthalein	Methyl orange
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
1	1.0	13.0	8.0
2	1.46	17.0	10.0
3	1.76	21.0	15.0
4	1.83	22.0	17.0
5	1.98
6	2.70	26.0	20.5
7	2.80	29.0	23.5
8	3.32	33.5	26.0
9	3.26	34.0	27.1

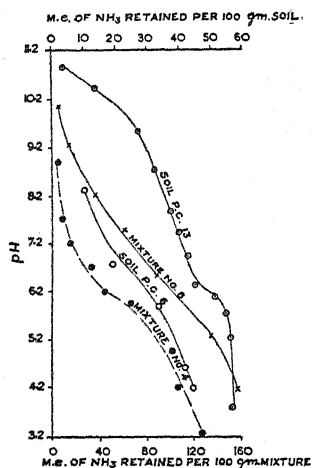


FIG. 6. AMMONIA ABSORPTION AT DIFFERENT pH VALUES BY SOILS AND FERROALUMINOSILICATES

ammonia retained by a mixture is equivalent to the $T/2$ value for that mixture. Similar results with soil acidoids were obtained by Puri and Asghar (13). The ferroaluminosilicate mixtures thus resemble soils in another respect, and this further supports the contention that in soils we are dealing with similar compounds.

The reaction between ammonia and the ferroaluminosilicate acidoids or that

between ammonia and soil acidoids thus is in no way different from the reaction of ammonia with true acids. The $T/2$ value corresponds to the base-exchange capacity, which is the same as the base-neutralizing power of the acidoid and, therefore, must be equal to the amount of ammonia or any other base that is required to neutralize the acidoid. On this assumption, if acidoid is partly neutralized with one base it should require a correspondingly small amount of another base for complete neutralization. To study this aspect of the problem, two silicate mixtures were neutralized partly to varying degrees by shaking with NaOH for 48 hours, after which the pH value as well as the ammonia absorption of the partly neutralized material was determined. The results are plotted in figure 6. The curves have the characteristics of residual titration curves. Ammonia absorption is thus a function of the pH value. Similar curves obtained with two soils are also included in figure 6 for comparison and to complete the analogy between artificial ferroaluminosilicates and natural soils.

SUMMARY

Some physicochemical properties of laboratory-prepared mixtures of iron and aluminum silicates of varying compositions have been studied. These mixtures were found to resemble soil colloids in all essential respects. For instance, clay and ultraclay can be produced from the silicates in the same way as in soils. Moisture absorption curves and titration curves of the silicate mixtures are no different from similar curves of soil colloids. Furthermore, the acidoids in the mixtures can catalyze hydrolytic reactions in the same way as do soil acidoids or even true acids. The amounts of ammonia absorbed by the mixtures are equivalent to their respective base-neutralizing powers, just as is the case with soil acidoids or with true acids.

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AN INTERPRETATION OF THE MOISTURE CONTENT-SURFACE FORCE CURVE FOR SOILS¹

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The progress that has recently been made in the study of the energy relationships in the soil-soil moisture system focuses attention upon the characteristics of the conventional moisture content-vapor pressure curves for such systems. It would appear that the curve showing the relationship between the moisture contents in a soil and the corresponding aqueous vapor pressures or relative humidities, should give a more complete expression of energy relationships, over the whole range of moisture contents, than could be obtained by any other experimental approach.

For practical use by the student of plant and water relations, the upper arm of the curve is of greatest significance. Since conventional methods involving constant relative humidities do not lead to great precision when relative humidities above 98 per cent are involved, better methods using some function of the surface force involved have been devised for this range (18, 20). Moisture contents within this narrow range of humidities are of unquestioned importance, but the entire range of moisture contents and their corresponding vapor pressures must be examined for a true understanding of the forces involved.

Experimental methods for locating the vapor pressure curves for soils have improved continuously since the early work of Shull (21) which suggested the possibility of bringing samples of soil into equilibrium with the atmospheres over sulfuric acid of varying concentrations. The methods and results of Thomas (22, 23) and of Puri, Crowther, and Keen (15) are familiar to all students of the subject. More recently Edlefsen (5, 6) and Alexander and Haring (1) have used other methods to achieve the same end.

As has been pointed out by Bodman and Edlefsen (3), the results of all these workers have been similar. A typical example of a moisture content-vapor pressure curve, from local work, is given in figure 1. In general, such curves seem to consist of three sections. When moisture content is plotted on the horizontal axis, and vapor pressure, or relative humidity, on the vertical axis, the first section curves upward, the middle section is essentially straight, and the third is concave downward, approaching saturation for the soil sample as the relative humidity approaches 100 per cent (16).

Despite the effort spent in locating these curves for various soils and soil separates, the curves have remained empirical. They can be used to express only the relationship between the variables which existed at the time of the ob-

¹ Published by permission of the director of the Hawaii Agricultural Experiment Station as Technical Paper No. 117.

² Collaborator, Hawaii Agricultural Experiment Station.

servation. Little progress has been made in identifying the factors that affect that relationship.

Although, as Veihmeyer and Edlefsen (24) indicate, the energy necessary to remove water from the soil is a continuous function of soil moisture, it is not necessarily true, as Baver (2) points out, that there is no change in the nature of the forces which are responsible for holding water in the soil at various moisture contents.

Several isolated observations seem to substantiate the belief that the forces involved in holding water in a soil at low vapor pressure may not be the same as those primarily involved at high vapor pressures. For example, Puri, Crowther, and Keen (15) note that temperature has but little effect in locating the curve within the range of high relative humidities but is a dominant influence in the

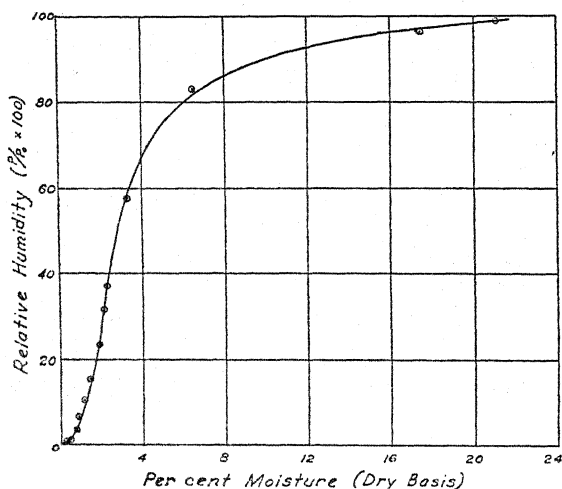


FIG. 1. A TYPICAL MOISTURE CONTENT—RELATIVE HUMIDITY CURVE FOR A SOIL FROM THE HILO COAST, HAWAII

lower range. Thomas (23) has reported that a soil saturated with sodium adsorbed less water at a specific, low vapor pressure than when saturated with calcium. At higher vapor pressures this relationship was reversed. Alexander and Haring (1) plotted the log. log. of the reciprocal of the relative humidity against the corresponding moisture content for four markedly different soil colloids and obtained curves which they interpreted as straight lines over wide ranges of moisture contents. This would hardly be expected if a single physical process were involved.

Although none of these, in itself, would convincingly challenge the concept that a single process, or force, was responsible for the observed relationship between surface forces and soil moisture contents, together they raise the question whether two or more separate processes may not be acting simultaneously. In our conventional soil moisture determination we may be measuring the sum-

mation of the moistures held in these various aspects and be unable to distinguish their individual contributions.

It is the purpose of this paper to suggest a hypothesis which may explain the aforementioned observations and at the same time conserve the usefulness of the moisture content-surface force curve.

THE BASIC HYPOTHESIS

It is suggested that the moisture in the soil, at any moisture content may be divided into two general classes upon the basis of the nature of the forces by which the water is held. Water in one of these classes is tightly held by forces of surface adsorption, by the hydration of ions on active surfaces, by the crystal surfaces of the soil minerals [if water, subject to loss at 100° C., such as the planar water of Kelley, Jenny, and Brown (11), is incorporated with them], and by some aspects of the moisture sorption of organic matter. For convenience these several processes are grouped under McBain's (13) term "chemosorption." This concept of tightly held moisture is not new. Pierce (14) has suggested that part of the water absorbed by textiles is held by tight chemical bonds while another part is loosely held. Gortner (8) finds the concept of "bound water" of value in interpreting a wide variety of experimental data. Water in the other category is condensed in the fine pores in the soil material. In large measure such water may be loosely held but it may appear in large amounts in fine-grained materials. It increases rapidly in amount as the relative humidity increases. It is water of this sort that approaches an infinite percentage of soil moisture, on the dry basis, as the relative humidity approaches 100 per cent. This water is said to be water of capillary condensation.

In answer to critics who had failed to obtain experimental support of his theory of surface adsorption, Langmuir (12) directed attention to the necessity of differentiating between adsorbed water and capillary-condensed water.

Chemosorption

It is evident that the curve showing the relationship between the moisture contents resulting from chemosorption must, with our present knowledge, be empirical. Each of the possibilities for chemosorption which has been mentioned may contribute to it. The best we can do is to group these contributions together and plot the sum against the corresponding vapor-pressure. In some materials base hydration may dominate the relationship; in others, surface adsorption may be most important. But with any specific sample it is suggested that a single smooth curve may be used to express the relationship between the moisture held by chemosorption and the vapor pressure.

Although many expressions for the relationship between the amount of material held by surface adsorption and equilibrium pressures have been suggested, both Bray and Draper (4) and McBain (13) hold that the Williams-Henry (10) equation is the most critical.

These workers report that results of simple surface sorption can be expressed by the relationship

$$\log (x_1/p) = K_1 - K_2 x_1$$

where x_1 = mass of material held per unit mass of adsorbent, p = the equilibrium pressure, in any convenient unit, and K_1 and K_2 are constants.

Granting the validity of this criterion permits its use in identifying the existence and magnitude of chemisorption in experimental work, since $\log(x_1/p)$ when plotted against x_1 , should give a straight line as long as processes of chemisorption alone have been involved. A serious departure from the straight-line relationship would suggest the introduction of some other process of moisture accumulation or a modification of the surface characteristics. An example of the form of the Williams and Henry curve, with arbitrary constants, is given in figure 2.

It is apparent that the application of the Williams-Henry criterion to sorption in soils assumes that the absorbent is constant with respect to exposed surface

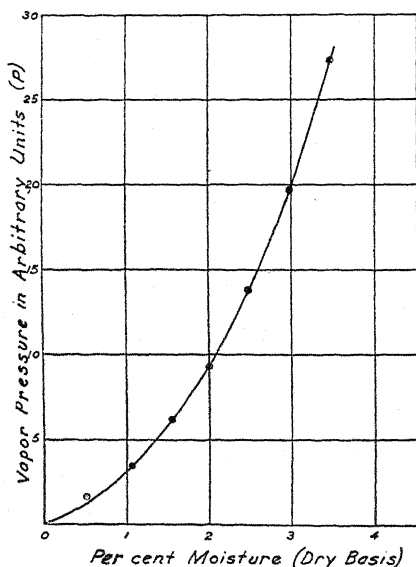


FIG. 2. THE CHARACTERISTIC FORM OF THE CHEMOSORPTION CURVE, ACCORDING TO WILLIAMS AND HENRY (10)

during the range of the critical observations. Swelling with concomitant re-orientation of ultimate particles and a probable modification of active surface would evidently warp the relationship. This assumption is discussed in the section on "Internal configuration and changes in microstructure."

Capillary condensation

It is evident from figure 2 that processes of chemisorption alone, cannot result in the large amount of water held in soils at high, or even at moderate, relative humidities. Moreover, it is apparent that the form for the curve of chemisorption does not express experimental results.

It is well known that water vapor, under proper circumstances, may condense in the small and irregularly shaped pores between adjacent grains.

Regardless of their configuration, these masses of condensed water are bounded,

at the air-water interfaces, by films, the curvatures of which are dependent upon the relative humidities. If chemisorption be disregarded, temporarily, it is evident that certain definite moisture contents, in a constant soil mass, must be associated with specific relative humidities, since these relative humidities control the curvature of the films which span the pore spaces, or bound the anchor rings, and these in turn limit the amount of water held behind them.

English workers (9, 27) have been active in studying the relationship between the moisture contents in a system of spherical particles, the form of the complex air-water surfaces at the interfaces, and the relative humidities with which such interfaces would be in equilibrium. The work of Fisher (7) in conjunction with that of Schofield (19) permits the computations of the relationships between

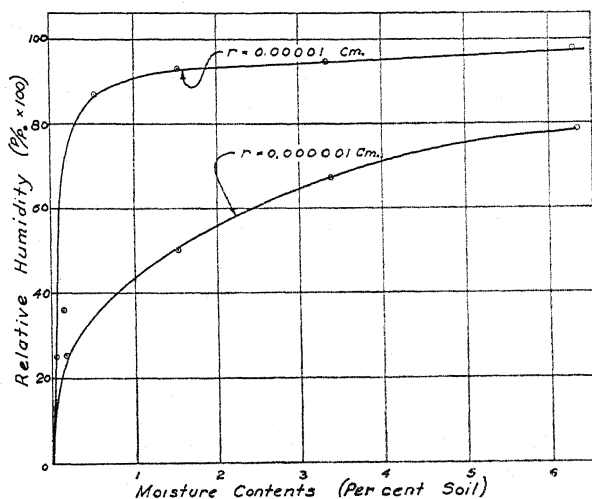


FIG. 3. MOISTURE ACCUMULATION BY CAPILLARY CONDENSATION, BASED ON FISHER'S (7) ANALYSIS

moisture contents resulting from condensation in the "ideal soil" of the English workers, and the corresponding relative humidities.

Two curves obtained in this way are shown in figure 3.

It is to be noted that Fisher's data end, for the hexagonal packing illustrated in figure 3, when the moisture content has increased to 6.3 per cent on the volume basis. There is no thought that water ceases to accumulate, by condensation, when this moisture percentage is reached. But at this moisture content, adjacent films would coalesce, by Fisher's analysis, creating a pattern of air-water interfaces which is of great complexity and which has never been examined.

On the other hand Bray and Draper (4) and McBain (13) emphasize the condensation of water in the pores between adjacent grains and set up an expression showing the maximum pore size which will permit an accumulation of water by condensation, for specific vapor pressures.

For the present purpose it is necessary to emphasize one important difference between these points of view. It is apparent, from the Haines' (9) interpreta-

tion, as well as from figure 3, that the accumulation of water by capillary condensation may begin with the first increment of vapor pressure, although the rate of accumulation of moisture at low vapor pressures may be small. Bray and Draper (4) hold that a threshold value for relative humidity must be reached before capillary condensation can occur.

Either of these processes would result in an accumulation of water, with increases in relative humidity, similar in general form to the relationship shown in figure 3. The only qualitative difference would be that the Bray and Draper (4) concept would move the curves up in the axes and give finite values for the relative humidity at 0 per cent moisture.

Since the shape, dimensions, and arrangement of the ultimate soil particles in a soil mass are not known, nor are these characteristics necessarily constant, it is impractical to attempt a mathematical presentation of the relationship between relative humidity and the amount of water held by capillary condensation. Such an equation would of necessity be empirical, regardless of the precision with which the observed points coincided with the computed curve.

Despite its quantitative uncertainty, the curve for capillary condensation, if plotted in such coordinates as shown in figure 1, would be concave as viewed from below. It would be complementary to that for chemisorption, and the two together would form the characteristic sigmoidal curve which has been observed so often with soils.

EXPERIMENTAL

The apparatus

It is evident that a convincing demonstration of the independent contributions of chemisorption and of capillary condensation to a series of observed soil moisture contents must be based on the development of an experimental technique which will permit the location of the curve for chemisorption at low vapor pressures. When soils are used, the inception of measurable capillary condensation is to be expected at low relative humidities. Consequently the apparatus used must permit the location of many equilibria within a narrow range of low vapor pressures.

None of the devices which has been used in work of this sort seemed adequate. The apparatus which was finally developed in the laboratories of the University of Hawaii³ permits an evaluation of the moisture content in the soil sample at any time, by an observation of the total mass of the sample, which is of known dry weight. This is done by suspending the sample in light pans from a sensitive Jolly balance spring. Routine observations of elongation are made with a cathetometer reading to 0.01 cm.

Springs of special alloy are used. These give an elongation of about 5 cm. per

³ The first unit was designed and constructed by Edward Inn in partial fulfillment of the requirements in the degree of master of science in physics. (Unpublished thesis, "An apparatus for measuring vapor pressure—moisture content relationships," 1942, on file at the University of Hawaii.)

gram. The calibration of the springs has not changed over long periods of continued use. Readings of weight to within 0.002 gm. are possible. Two grams of sample can be loaded on the three-stage pans which are designed to increase the surface exposure. Moisture percentages are probably accurate to within 0.1 per cent.

Readings of pressure at equilibria are made by observations upon a manometer similar to that used by Alexander and Haring (1). In the local design the manometer was lengthened to allow the use of a light oil or other liquid in place of mercury. Two materials have been used successfully for piezometric liquids: one of these, Apiezon B, is frequently used in oil diffusion pumps; the other, Arochlor 1248, was obtained from the Distillation Products, Inc. When either of these materials is used and observations are made with the aforementioned cathetometer, vapor pressure measurements may be made with an accuracy equivalent to 0.01 to 0.02 mm. of mercury.

In assembly, the spring, carrying the pans at its lower end, hangs from the top of a 2-inch glass tube about 24 inches long. The bottom is sealed with a glass plate. A manifold from this tube leads to one arm of the long manometer suitably filled with oil. The other arm of the manometer leads to a large expansion flask. A side tube from the manifold permits the addition of water vapor to the spring chamber, by the vaporization of water from an air-free water reservoir. Water vapor can be withdrawn from the spring chamber by a rotary oil pump. Hence the apparatus can be used to trace the relationship between soil moisture and vapor pressure when the sample is being wetted by additions of water vapor, or as it is being dried by intermittent evacuation. A by-pass permits the simultaneous evacuation of the spring chamber, the expansion flask, and the two arms of the manometer at the beginning of a series of observations. Subsequently differences of pressure, as measured on the manometer, are reported as measures of the aqueous vapor pressure over the soil sample. All necessary stopcocks are mercury-sealed.

In operation, the sample of soil is distributed evenly over the three pans; the apparatus is sealed and evacuated to a pressure of less than 10^{-3} mm. of mercury. The by-pass into the expansion flask is closed, and the weight of the sample in equilibrium with zero vapor pressure is noted. A small amount of water vapor is admitted to the spring chamber by a brief opening of the valve leading to the water reservoir. In general, equilibrium is attained in about 4 hours, although longer periods are necessary for the higher vapor pressures. At the end of the period the new weight is noted, as well as the pressure difference as measured on the manometer. All observations are made with the same cathetometer.

Careful temperature control is obviously imperative. Significant parts of the apparatus are submerged in a water bath equipped with a long stirring shaft with sets of three propeller-like blades, a bayonet-type electric heater, and a large homemade thermoregulator containing mercury and toluene. The contact between the mercury and platinum, in this device, is protected with a thin layer of mineral oil. When used with an adequate electric relay, temperature control

within 0.01°C . can be obtained. Figure 4 is a diagrammatic sketch of the apparatus.

Typical results

Two assemblies similar to that described above have been in continuous operation for almost 3 years. During this time many soil samples and other materials have been studied. Some of these were size-separates from local soils, others were originally identical samples and were used to note the effects of temperature upon the two hypothetical processes of water sorption; other samples were treated with different bases to note the effect of replaceable cations upon the characteristics of water sorption.

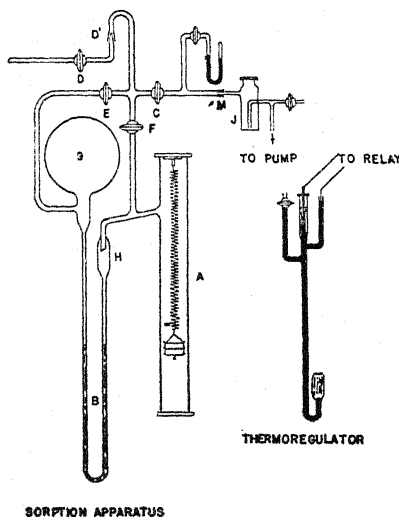


FIG. 4. SORPTION APPARATUS AND THERMOREGULATOR

In general, results have been similar. All have yielded to an analysis designed to differentiate between the contributions of chemisorption and capillary condensation. The inevitable differences which exist between the results obtained from such varied materials, as well as changes in external factors, seem to be in degree and not in kind.

In the analysis, contributions by chemisorption were identified by use of the Williams-Henry criterion. Moisture in the soil, at any specified relative humidity, in excess of that required by the criterion was assumed to be water of capillary condensation. Bray and Draper (4) used the same method, although their experimental points were too few to do more than illustrate the abrupt change of character in the curve when capillary condensation became significant.

This analysis, as applied to a soil sample from the Hilo coast on the Island of Hawaii, is given in some detail to illustrate the method used. The raw data and the evident computations are given in table 1.

As has been indicated, the Williams-Henry criterion holds that $\log (x_1/p)$ and x_1 should exhibit a straight line relationship as long as the processes of chemosorption alone are involved. These variables are plotted in figure 5. The evidence of a rectilinear relationship within the range of lower moisture contents is apparent. Here the correlation coefficient between x_1 and $\log (x_1/p)$ for the first thirteen equilibria noted in table 1, and plotted in figure 5, is -0.931 .

TABLE 1

Experimental results and computations of moisture content due to chemosorption and to capillary condensation in Hilo Coast soil

(First wetting curve)

EQUILIBRIUM NUMBER	MOISTURE CON- TENT x_1	VAPOR PRESSURE p^*	$\frac{x_1}{p}$	$\log \frac{x_1}{p}$	$(p/p_0) \times 100^\dagger$
	<i>per cent</i>				
1	0.10	0.08	1.25	+0.10	0.18
2	0.31	0.14	2.21	+0.34	0.31
3	0.52	0.23	2.26	+0.35	0.52
4	0.83	0.38	2.18	+0.34	0.85
5	1.14	0.55	2.07	+0.32	1.24
6	1.45	0.87	1.67	+0.22	1.96
7	1.76	1.30	1.35	+0.13	2.92
8	2.27	2.06	1.10	+0.04	4.63
9	2.79	3.32	0.84	-0.08	7.46
10	3.20	4.08	0.78	-0.11	9.17
11	3.62	4.97	0.73	-0.14	11.17
12	4.13	6.67	0.62	-0.21	14.99
13	4.55	8.11	0.56	-0.25	18.22
14	5.47	10.95	0.50	-0.30	24.61
15	6.82	16.13	0.42	-0.38	36.25
16	7.96	30.79	0.38	-0.52	46.72
17	9.19	25.99	0.35	-0.46	58.40
18	10.45	29.86	0.35	-0.46	67.10
19	11.67	34.21	0.34	-0.47	76.88
20	13.22	37.36	0.35	-0.46	83.96
21	14.77	40.18	0.37	-0.43	90.29
22	16.63	42.60	0.39	-0.41	95.73
23	17.87	43.69	0.41	-0.39	98.18
24	19.94	44.30	0.45	-0.35	99.62

* p is given in centimeters of Apiezon B.

† p_0 (at $28^\circ\text{C}.$) = 44.5 cm.

Although the number of observations within the critical range is small, this high value for the correlation coefficient is highly significant. If this correlation coefficient is accepted as evidence of a rectilinear relationship between x_1 and $\log (x_1/p)$, and if the Williams-Henry criterion is adequate, it is apparent that the first thirteen points in the Hilo soil series represent a process of chemosorption alone.

If we assume that the first thirteen points given in table 1 follow the Williams-

Henry law, we can establish the equation for this aspect of the sorption process. By the method of normal equations we obtain

$$\log (x_1/p) = 0.42 - 0.146 x_1$$

as the best fitting straight line for the points in question.

This curve, with the vapor pressure expressed as a relative humidity, as is usual, is given in figure 6. Here circled points are the actual observations; x_1 represents the hypothetical contributions from chemisorption; values of x_2 represent contributions from capillary condensation which were obtained as differences. Although the curve for x_2 , in figure 6, may be closely approximated by an exponential expression, no attempt has been made to evaluate it as an empirical form for reasons that have been given.

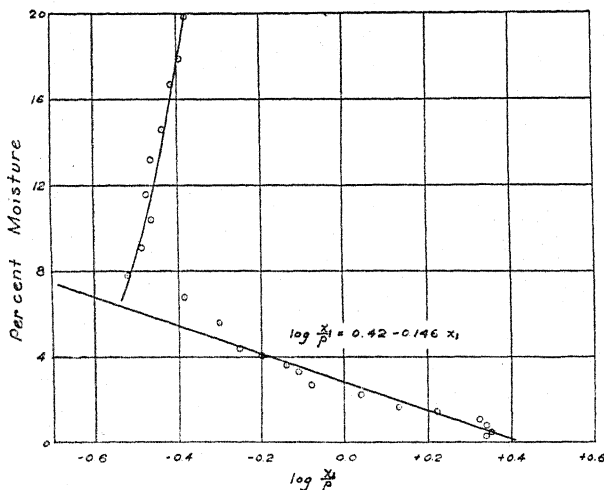


FIG. 5. THE WILLIAMS-HENRY CRITERION FOR CHEMOSORPTION AS APPLIED TO RESULTS FROM A HILO COAST SOIL

It is to be noted that capillary condensation in the Hilo soil is first apparent when the relative humidity is about 18 per cent.

It is evident that this type of analysis is possible only if the experimental data are rich enough to provide several, if not many, points in the range of chemisorption. Not many results of experimentation with soils have been found in the literature which permit this statistical attack. It is probable that the four series of observations reported by Alexander and Haring (1) are richest in observations at low vapor pressures. These series add strength to the argument; only the observations on the Cecil and the Miami colloids give enough experimental points at vapor pressures below that marking the inception of capillary condensation to give quantitative support. This work involved drying wet soil samples. Consequently the experimental points trace the drying arms of the curves.

Each of these soil materials was reported in sufficient detail to provide nine points on the desorption curves after capillary condensation had ceased to be important. The correlation coefficient between x_1 and $\log (x_1/p)$ is -0.783 for the Cecil colloid and -0.970 for the Miami colloid.

Other examples, taken from the long list of local studies are given in table 2. The soil material used was the colloidal separate from Superior clay loam. Two

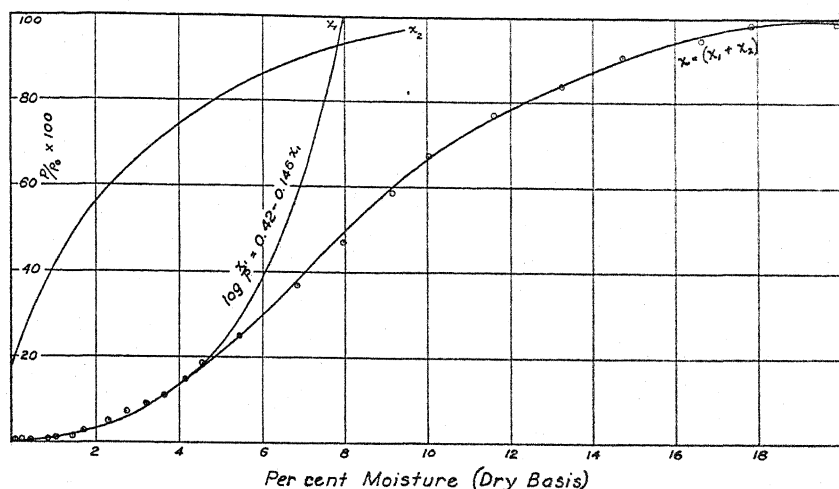


FIG. 6. ANALYSIS OF OBSERVATIONS ON HILO COAST SOIL

Circled points are actual observations. Curve marked x_1 is hypothetical contribution by chemisorption; x_2 is hypothetical contribution by capillary condensation.

TABLE 2
Results with superior clay loam colloid

SYSTEM	NUMBER OF OBSERVATIONS WITH RANGE OF CHEMOSORPTION	CORRELATION COEFFICIENT x_1 and $\log (x_1/p)$
Hot		
Wetting.....	16	-0.872 ± 0.06
Drying.....	13	-0.704 ± 0.09
Cold		
Wetting.....	7	-0.897 ± 0.05
Drying.....	6	-0.967 ± 0.02

series are reported. One was held at a constant temperature of 32.70°C. , the other at 17.20°C. Each series was kept under detailed observation while the sample was being wetted and while the sample was being dried by successive evacuations.

Effects of temperature

Under the terms of the hypothesis, water in an unsaturated soil is held by two dissimilar processes. In the case of chemisorption, water is held by surface

activity and, in a specified case, the amount of water held is directly, and rationally, related to the aqueous vapor pressure with which the soil is in equilibrium. On the other hand, water may be condensed between adjacent grains and held under the curved air-water interfaces. The amounts of water so held are governed by the curvatures within these interfaces. These curvatures are rationally related to the relative humidities with which the samples are in equilibrium.

Plotting equilibrium pressures, in term of relative humidities, against moisture contents, within the range dominated by chemisorption, adds a factor which does not appear to be pertinent to the physical process involved. On the other hand, the use of values of relative humidities at higher moisture contents where capillary condensation is dominant would tend to minimize the effects of temperature.

Consequently, if the basic hypothesis is adhered to, differences of temperature should affect more significantly at low moisture contents than at high moisture contents the position of a curve showing the relationship between moisture contents and relative humidities. Reference to the observations by Puri *et al.* (15) has already been made.

This corollary to the general hypothesis was explored in two assemblies operating at different temperatures. One of these carried the conventional heating element and operated at 32.70° C. In the other, the thermoregulator was so installed that cold water, from an electrically cooled water-bath, was injected into the tank when the temperature exceeded a critical value. The average temperature in the cold bath for 23 observations was $17.20^{\circ} \pm 0.08^{\circ}$. Apiezon was used as a manometric material in both cases. Observations with a pycnometer upon the density of this material gave a value of 0.881 gm. per cubic centimeter. This density was not significantly affected by temperature differences within the range under observation.

Results of one series of observations made upon a soil colloid extracted from Superior clay loam are given in figure 7. Here the ordinate is given in terms of vapor pressure. Observations on the hot series were limited by the length of the manometer to pressures below 47 cm. of Apiezon. Inspection indicates that, at any comparable high vapor pressure, more water is held at the lower temperature. This difference disappears when the vapor pressure is low.

When the same data are replotted in terms of relative humidity, as is done in figure 8, the situation is reversed. At low relative humidities, the moisture held at a given value is consistently less in the cold series than in the hot series. This difference becomes less apparent, and perhaps insignificant, at higher humidities.

This observation is contrary to that reported by Puri *et al.* (15) who find that "in atmospheres of low humidity the relative vapor pressure increases considerably with increasing temperature until at the lowest humidity studied the relative vapor pressure is almost doubled by a 20° rise of temperature." It is evident that the method used by the English workers is quite different from that used in the present studies.

A necessary assumption in Henry's derivation, for chemisorption, is that the absorbent material be comparable in all respects throughout the scope of the analysis. Changes in microstructure, as a result of a changing temperature,

might modify the character of the absorbent material with more significant effect upon the amount of water held by chemisorption than would be indicated by an evaluation of the constants in the basic equation (10) at the two temperatures.

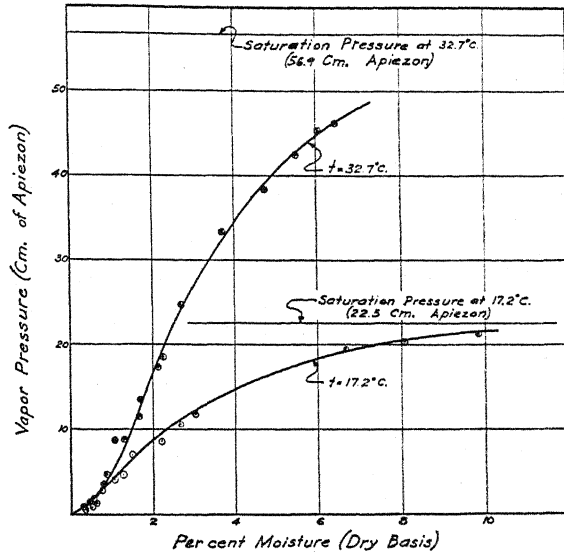


FIG. 7. EFFECT OF TEMPERATURE ON WATER SORPTION BY A SOIL COLLOID
Note that the ordinate is in terms of vapor pressure, not relative humidity

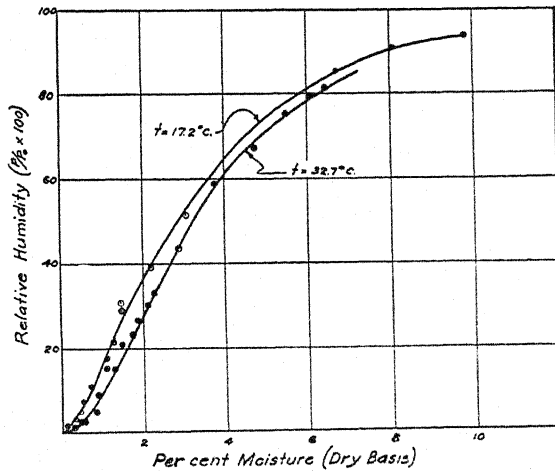


FIG. 8. EFFECT OF TEMPERATURE ON WATER SORPTION BY A SOIL COLLOID
Here the ordinate is in terms of relative humidity

Internal configuration and changes in microstructure

During the course of the studies here reported in part, a growing conviction has developed in this laboratory that soil samples are not stable materials but

respond with structural changes to temperature and to modification of moisture content in such measure that recognition must be given to these effects. At present, such allowance must be qualitative only. There is little evidence yet of the nature or magnitude of changes of internal configuration in a soil sample with changes in either of these conditions. A technique by which the actual volume and microstructure of a soil, together with its adherent water, might be studied with respect to changes of temperature or of moisture content, would be of great value.

Work with other materials provides concepts which find qualitative support in the suggested relationships. For example, McBain (13) points out that charcoal expands with the sorption of water or other materials. Moreover, the sorption of such an inert material as carbon dioxide upon charcoal results in an expansion which is dependent upon temperature. Expansion, under comparable conditions, was greater at low temperatures than at high temperatures.

Some such structural modifications may be apparent in soils. And if this is true, observations on soil samples which were originally identical may not be comparable if made at different temperatures, for by the simple change of temperature we may have changed the internal configuration with far-reaching effects. And if swelling is significant with the sorption of water, a series of observations at varying moisture contents may not be strictly comparable. McBain (13) discusses this possibility, in considerable detail, as "steric hindrance."

Some qualitative support for the concept that soils and soil separates suffer some microstructural modification is provided in previous papers (25, 26) dealing with the evolution of heat in a moist sample of soil when temperature reductions are involved. The effect was not observed when the samples were either oven-dry or at maximum field capacity. The hypothesis suggests that the cooling of the partly wet sample results in structural change and in the exposure of potential sorption areas which were previously drier than the rest of the sample. The readjustment of moisture to attain equilibrium would probably result in a measurable overall loss of heat.

In this regard, McBain (13) suggests that it is improper to assume "that the equilibriums at two temperatures are identical in nature and that the solid phase has the same composition at both temperatures, differing only in temperature and in the external equilibrium gaseous pressure to which it is submitted."

One example of the possible influence of surface and structural modifications with wetting and drying is provided by vapor pressure studies with Ca^{++} - and Na^{+} -saturated colloidal material which was extracted from Superior clay loam. These materials were studied at 35° C. in the vapor pressure apparatus that has been described. The colloids were put on the pans, and the apparatus was sealed and evacuated for 2 hours. Water vapor was then introduced in small increments until a vapor pressure of about 5 cm. of arochlor⁴ had been established. The samples were then dried by intermittent evacuation, and the process was repeated. After four such cycles for the Ca^{++} -colloid and three for the Na^{+} -colloid, the wetting was allowed to continue to near saturation, and the colloids were

⁴ Density of arochlor (1248) at 35°C. is 1.44 gm. per cubic centimeter.

then dried by intermittent evacuation, as is normally done in tracing the hysteresis curve.

Results are given in figures 9 and 10. It will be noted that the preliminary Na^+ -curves practically, and probably within the limits of precision available, retrace themselves as the material is wetted and dried. On the other hand, the Ca^{++} -colloid, after the first cycle, exhibits the unexpected and, so far as is known, the unreported characteristic of holding less moisture on the drying arm than on the wetting arm, for a given vapor pressure.

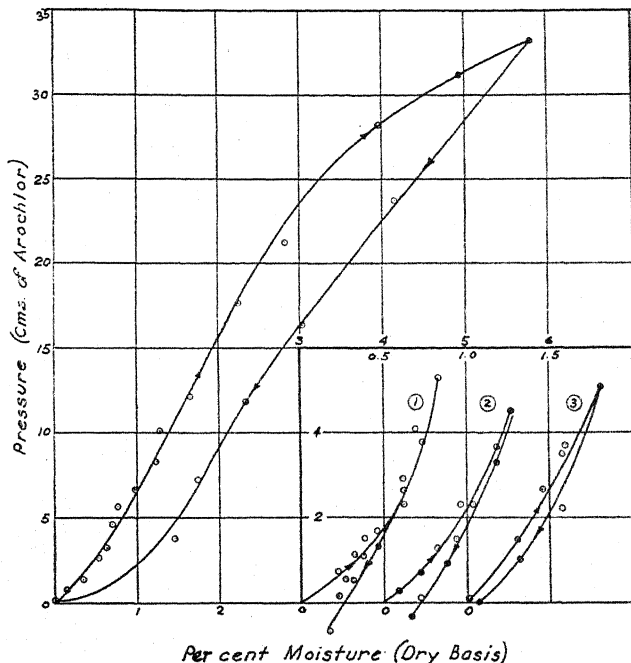


FIG. 9. THE HYSTERESIS LOOP WITH Na^+ -SATURATED COLLOID AFTER THREE PRELIMINARY WETTINGS

Details of preliminary wettings given in inset. Coordinates of inset as in main figure but on given scale.

When the range of wetting is extended, the Na^+ -colloid exhibits a typical hysteresis loop, whereas the loop of the Ca^{++} -colloid seems to shrink to insignificance. There is no thought that all soil materials treated in this way would exhibit this characteristic. The observations are given in some detail to illustrate the complexities which have frequently arisen. Such results have tentatively been ascribed to modifications of the adsorbing surfaces.

It is interesting to note in this connection that Edlefsen (5) failed to find evidence of hysteresis in a sample of soil that had been wetted and dried before quantitative observations were begun.

Somewhat analogous results were obtained by Rao (17), who worked with such

pure materials as the chemically prepared oxides of Ti, Fe, Al, and Si in an apparatus similar to that described above. Rao reports that the upper end of the hysteresis loop for these materials is permanent and reproducible after the completion of about five wetting and drying cycles. When this condition exists, the early wetting curve and the late drying curve are coincident. The suggestion is that the dry end of the hysteresis loop marks the beginning of accumulation of water through capillary condensation. It is interesting to note that Rao attributes the inversion, in his basic curves, to a change from monomolecular sur-

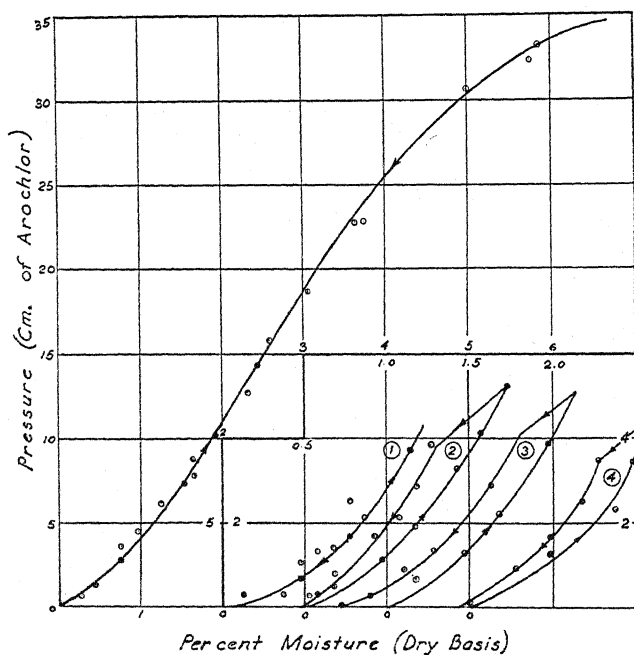


FIG. 10. THE HYSTERESIS LOOP WITH Ca^{++} -SATURATED COLLOID AFTER FOUR PRELIMINARY WETTINGS

Details of preliminary wettings given in inset

face adsorption, as identified by the Williams-Henry criterion, to accumulation by capillary condensation.

The brief description of results in this section on structural modification is not intended to provide the basis of a clear understanding of the complexities of sorption possibilities or of structural changes in soil samples as they experience modifications of temperature and soil moisture histories. Its purpose is to focus attention on the many variables involved in a study of the relationships between soil moisture and functions of surface energy.

It seems clear, however, that the vapor pressure curve is not specific for a soil or for a soil separate. And if this is true, the significance of the capillary potential, as a single-valued function of soil moisture, may be open to question.

SUMMARY

The conventional sigmoidal form of the curve expressing the soil moisture-vapor pressure relationships for soils and soil separates is assumed to result from two independent processes which may be operating concurrently.

One of these, which dominates the action at low vapor pressures, is a process of surface adsorption and is thought to follow the Williams-Henry law for monomolecular adsorption.

At higher vapor pressures water condenses in interstices between grains. The water accumulates rapidly as the vapor pressure approaches saturation for the given temperature.

No experimental procedures permit the evaluation of these contributions during the determination of the curve's position; but mathematical analysis permits a distinction when the entire array of experimental points is available for study. Such analysis gives considerable assurance to the thought that sorption at low vapor pressures satisfies the Williams-Henry criterion.

There is some evidence that the vapor pressure-moisture content curve is not a specific characteristic for a soil or a soil separate. Apparently the temperatures involved and the previous soil moisture history conditions the material in such a way that the position of the curve in the axis depends partly, at least, upon how the sample has been treated.

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PHOSPHATE FIXATION BY SOIL MINERALS: II. FIXATION BY IRON, SILICON, AND TITANIUM OXIDES

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Some of the aspects of phosphate fixation by mica and related mineral groups was covered in the first paper of this series (5). The present paper is an extension of that work and includes a study of phosphate fixation by some of the metallic oxides that appear as soil minerals. The minerals studied were hematite, limonite, magnetite, rutile, quartz, and ilmenite.

The methods used for studying phosphate fixation were the same as those reported in the aforementioned paper and briefly are as follows: Five grams of mineral, ground to pass a 100-mesh sieve by means of a mullite mortar and pestle, was mixed with water, sodium hydroxide or hydrochloric acid to adjust the pH, and orthophosphoric acid. The mixture was shaken overnight in an end-over-end shaker running at 6 r.p.m. in a constant temperature room at 25°. The material was centrifuged, and the phosphate fixed was determined by the difference between the amount added and that left in solution. The phosphorus was determined by the coeruleomolybdate method as improved by Atkins (1). The data recorded in the tables give the amounts of phosphate fixed by 5 gm. of mineral in 25 ml. of solution. This weight-volume relationship was always maintained. The solution volumes given in the tables are milliliters of 0.2 *N* NaOH, 0.2 *N* HCl, and H₃PO₄ (1.7770 gm. per liter) and are reported on this basis even though stronger solutions may have been used to hold the volume to 25 ml.

All of the oxide minerals studied, except silica, had a hardness definitely less than that of the mullite mortar and pestle. Silica was about as hard or possibly a trifle harder, and, therefore, was probably somewhat contaminated with mullite. No satisfactory method, however, of grinding the harder minerals, including the aluminum oxides, has been found.

The data collected for the seven oxides studied are presented in tables 1 to 8.

DISCUSSION

The mechanism of phosphate fixation has been studied and theorized upon by many writers. The data from this and the preceding paper (5) are summarized in table 8. It is evident that the naturally occurring minerals vary considerably in their ability to fix phosphate.

Minerals ground to pass a 100-mesh sieve (150- μ particles) show considerable variation in their ability to fix phosphate. The two varieties of hematite vary in this respect. Magnetite is entirely inert under the experimental conditions reported in this paper. Ilmenite (FeO-TiO₂) shows a mere trace of reaction with orthophosphoric acid, and rutile shows even less reaction. The inertness of

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magnetite is in accord with the statements of Mellor (3), who lists a large number of chemical compounds that will not react with magnetite. In table 9 are recorded the quantities of H_3PO_4 fixed per 100 gm. of iron in various iron-bearing minerals. If hematite reacted completely with phosphoric acid according to the equation $\text{Fe}_2\text{O}_3 + 2\text{H}_3\text{PO}_4 = 2\text{FePO}_4 + 3\text{H}_2\text{O}$ it would combine with 60 per cent of its weight of H_3PO_4 . The observed maximum of around 1 per cent fixed H_3PO_4 indicates that double decomposition is not complete under the conditions of the experimentation.

This variation in the amount of phosphate fixed by various iron-bearing minerals and by different varieties of hematite indicates that both the physical condition of the mineral and the chemical composition are important factors in phosphate fixation. The inertness of magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) and ilmenite ($\text{FeO} \cdot \text{TiO}_2$) in comparison with hematite (Fe_2O_3) and rutile (TiO_2) indicates that the mixed oxides tend to fix less phosphate than the straight oxides. The compactness of the atoms in the crystal structure is probably of great import-

TABLE 1
*Phosphate fixed by magnetite**

pH.....	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	H_3PO_4 (1.7770 GM. PER LITER)	
													ml.	T./A.
Phosphate fixedper cent	0	0	0	0	0	0	0	0	0	0	0	0		
0.2 N HCl-NaOH†														
.....ml.	2.2	1.8	1.5	1.3	1.0	0.7	0.5	0.3	..	0.2	0.3	0.5	2.5	2

* Phosphate fixed by 5 gm. of mineral, ground to pass 100-mesh sieve (150μ), in 25 ml. of solution.

† Underscored data represent milliliters NaOH.

ance in phosphate fixation. The total iron content of a mineral is not a criterion of phosphate-fixing capacity over a wide range of pH values.

The summarized data in table 8, which includes data in this paper and an earlier publication by Perkins and King (5), show that, of the several classes of minerals tested, those belonging to the mica group are the most active in phosphate fixation. The 100-mesh micas fix approximately six times as much phosphate as the most active of the 100-mesh iron minerals. These data are contrary to the preliminary theory of the authors. This opinion was based in part on publications by Metzger (4) and others who showed that the removal of iron and aluminum from the soil greatly decreased phosphate fixation. An explanation of this deviation is that Metzger and others were dealing with much more finely divided iron minerals, definitely in a different physical condition and probably in a somewhat different chemical form.

The greater reactivity of the 100-mesh micas with phosphate than of the iron oxides is probably associated with the more open crystal lattice. The average specific gravity of the micas is about 3, whereas the specific gravity of the hema-

TABLE 2
Phosphate fixed by hematite No. 1*

pH	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	H ₂ PO ₄ (1.7770 gm. per liter)	
													ml.	T./A.
Phosphate fixed..... per cent	100	100	100	100	100	100	100	100	†	†	†	†	2.5	2
0.2 N HCl-NaOH†..... ml.	8.0	4.1	2.2	2.0	1.8	1.3	0.8	0.1	0.2	0.5	†	†		
Phosphate fixed..... per cent	97	98	99	97	93	90	80	72	63	†	†	†	10	8
0.2 N HCl-NaOH..... ml.	5.0	3.5	2.0	1.7	1.3	0.6	0.2	0.2	†	†	†		
Phosphate fixed..... per cent	75	78	71	60	56	55	49	43	36	34	37	†	25	20
0.2 N HCl-NaOH..... ml.	2.3	1.3	1	0.3	0.5	1.4	1.7	2.0	2.4	3.0	3.9	†		
Phosphate fixed..... per cent	44	64	42	31	19	16	13	10	9	29	18	†	50	40
0.2 N HCl-NaOH..... ml.	1.7	1.0	0.3	1.3	2.4	3.1	3.7	4.4	5.0	6.0	7.0	†		
Phosphate fixed..... per cent	27	23	22	16	17	11	6	7	9				100	80
0.2 N HCl-NaOH..... ml.	2.2	3.5	4.8	5.6	6.4	7.0	7.8	9.0	11.0					

* Phosphate fixed by 5 gm. of mineral, ground to pass 100-mesh sieve (150 μ), in 25 ml. of solution.

† Underscored data represent milliliters NaOH.

‡ Material in suspension; reading unobtainable.

tite and magnetite is around 5 and that of limonite around 4. This may be interpreted as indicating a larger void space in the crystal-lattice structures of the micas than in that of the iron oxides. Speculation indicates that the increased phosphate fixation by the micas over the iron oxides may be due to the activity of the internal surface of the micas and the ability of the phosphate ion to reach this surface. This theory of phosphate penetration into the micas but not into the iron oxides is partly substantiated by the assumption that the gelatinous nature of the iron phosphate precipitate would result in coating of the hematite particles and prevention of additional interaction between phosphate and iron.

It may be assumed that if the minerals were ground much more finely, different results would be obtained. The particles of 100-mesh size, through an impalpable powder, are relatively large and have a limited external surface area. The

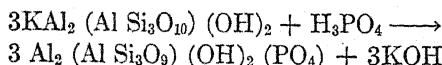
TABLE 3
*Phosphate fixed by hematite (R.O.)**

pH.....	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	H ₂ PO ₄ (1.7770 GM. PER LITER)	
													ml.	T./A.
Phosphate fixed per cent	9.0	25	65	78	76	65	59	60	57	49	46	0		
0.2 N HCl-NaOH* ml.	3.9	2.5	1.4	0.8	0.7	0.2	<u>T</u>	<u>0.1</u>	<u>0.2</u>	<u>0.3</u>	<u>0.4</u>	<u>0.8</u>	2.5	2
Phosphate fixed per cent	11	0	0	14	19	10	15	18	18	17	22	27		
0.2 N HCl-NaOH ml.	5	1.5	1	0	<u>0.5</u>	<u>0.6</u>	<u>0.8</u>	<u>1.0</u>	<u>1.1</u>	<u>1.5</u>	<u>1.8</u>	<u>2.0</u>	10	8

* Phosphate fixed by 5 gm. of mineral, ground to pass 100-mesh sieve (150 μ), in 25 ml. of solution.

† Underscored data represent milliliters NaOH.

same weight of mineral ground to 1.5 μ size instead of 150 would have 1,000 times greater surface area. In the case of a dense mineral with a structure of such a nature that the phosphate could not penetrate, the fixation would be limited to the external surface area. The data presented by Perkins and King (5) indicate that in the case of the mica and related groups of minerals, the reaction between mineral and phosphoric acid is associated with the substitution of Al for Si. If this is the case, a possibility for the reaction would be:



with the PO₄ radical somehow combining with the AlSi₃O₁₀ radical. The above reaction would unite one valence from each phosphoric acid group to each of the simplest mica units. If this represents the reaction between phosphate and mica, the mica would fix slightly over 8 per cent of its weight of H₃PO₄. A fixation of 6.84 per cent has been measured.

TABLE 4
Phosphate fixed by limonite*

pH	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	H ₂ PO ₄ (1.7770 gm. per liter)	
													ml.	T./A.
Phosphate fixed..... per cent	100	100	100	100	100	100	100	100	98	92	77	69	2.5	2
0.2 N HCl-NaOH†..... ml.	4.7	4.0	3.4	2.5	1.5	0.5	0.3	0.2	0.1	0.1	0.4	0.7		
Phosphate fixed..... per cent	95	95	89	81	79	75	62	56	?	?	?	?		
0.2 N HCl-NaOH..... ml.	2.0	1.3	0.7	0.1	0.1	0.3	0.4	0.5	0.6	0.8	?	10	8
Phosphate fixed..... per cent	57	58	58	58	57	56	47	30	19	14	8	1	25	20
0.2 N HCl-NaOH..... ml.	1.0	0.1	0.3	0.5	0.8	1.3	1.6	1.9	2.1	2.6	3.2	3.6		
Phosphate fixed..... per cent	11	17	19	46	43	21	5.0	3	16	17	12	7	50	4.0
0.2 N HCl-NaOH..... ml.	1.3	1.9	2.4	2.7	2.9	3.4	4.0	4.1	5.4	6.3	7.4		

* Phosphate fixed by 5 gm. of mineral, ground to pass 100-mesh sieve (150 μ), in 25 ml. of solution.

† Underscored data represent milliliters NaOH.

TABLE 5
Phosphate fixed by quartz*

pH.....	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	H ₃ PO ₄ (1.7770 GM. PER LITER)	
													ml.	T./A.
Phosphate fixedper cent	8	0	0	0	3	5	3	0	0	0	0	0		
0.2 N HCl-NaOH†ml.	1	0.5	0.3	0	0.05	0.10	0.13	0.18	0.21	0.28	0.38	0.45	2.5	2

* Phosphate fixed by 5 gm. of mineral, ground to pass 100-mesh sieve (150 μ), in 25 ml. of solution.

† Underscored data represent milliliters NaOH.

TABLE 6
Phosphate fixed by rutile, TiO₂*

pH.....	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	H ₃ PO ₄ (1.7770 GM. PER LITER)	
													ml.	T./A.
Phosphate fixedper cent	6	27	68	79	99	71	28	29	31	26	8	3		
0.2 N HCl-NaOH†ml.	2.25	1	1	0.9	0.8	0.5	0.1	T	<u>T</u>	<u>0.1</u>	<u>0.3</u>	<u>0.6</u>	2.5	2
Phosphate fixedper cent	27	35	41	39	41	44	39	19	15	7	2			
0.2 N HCl-NaOHml.	2.5	1.0	0.5				<u>0.2</u>	<u>0.3</u>	<u>1.1</u>	<u>1.4</u>	<u>1.5</u>		10	8
Phosphate fixedper cent	4	17	33	23	19	9	4	3	6	6	4			
0.2 N HCl-NaOHml.	1.8	0.9	0.5	<u>1.1</u>	<u>1.4</u>	<u>1.5</u>	<u>2.0</u>	<u>2.3</u>	<u>2.4</u>	<u>2.6</u>	<u>3.2</u>		25	20

* Phosphate fixed by 5 gm. of minerals, ground to pass 100-mesh sieve (150 μ), in 25 ml. of solution.

† Underscored data represent milliliters NaOH.

TABLE 7
Phosphate fixed by ilmenite, FeTi(O₂)*

pH.....	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	H ₃ PO ₄ (1.7770 GM. PER LITER)	
													ml.	T./A.
Phosphate fixedper cent	47	69	77	31	78	50	38	30	23	17	11			
0.2 N HCl-NaOH†ml.	2.7	1.0	0.5	0.25	0.2		<u>0.1</u>	<u>0.2</u>	<u>0.3</u>	<u>0.4</u>	<u>0.5</u>		2.5	2
Phosphate fixedper cent	36	31	36	36	28	25	22	20	16	11	5			
0.2 N HCl-NaOHml.	1.0	0.6	<u>0.1</u>	<u>0.2</u>	<u>0.4</u>	<u>0.5</u>	<u>0.7</u>	<u>0.9</u>	<u>1.1</u>	<u>1.3</u>	<u>1.5</u>		10.0	8

* Phosphate fixed by 5 gm. of mineral, ground to pass 100-mesh sieve (150 μ), in 25 ml. of solution.

† Underscored data represent milliliters NaOH.

The low fixation by quartz is to be expected from the characteristics of the mineral. The data for rutile are of some interest, but because of the small amount of titanium in soils the results are of little practical importance.

The fact that 100-mesh micas fix more phosphate than the 100-mesh iron minerals is not to be taken as evidence that in the soil the iron minerals are not a primary factor in phosphate fixation. Soils are made up of systems that are not comparable with pure minerals in water, and it is probable that in a soil the iron oxides exist as smaller-sized particles and that they coat the larger particles with a film of approximately monomolecular thickness. Some attempts have been

TABLE 8
*Largest amount of phosphate fixed by the several minerals**

H ₃ PO ₄ FIXED PER 100 GM. MINERAL		H ₃ PO ₄ FIXED PER 100 GM. MINERAL	
	gm.		gm.
Kaolinite†.....	0.28	Magnetite (Fe ₃ O ₄).....	0.00
Talc†.....	0.01	Hematite No. 1 (Fe ₂ O ₃).....	1.14
Pyrophyllite†.....	0.05	Hematite R.O. (Fe ₂ O ₃).....	0.07
Muscovite†.....	6.84	Limonite (2Fe ₂ O ₃ ·3H ₂ O).....	0.80
Phlogopite†.....	0.96	Quartz (SiO ₂).....	0.01
Biotite†.....	5.25	Rutile (TiO ₂).....	0.29
Margarite†.....	5.78	Ilmenite (FeO·TiO ₂).....	0.01

* All minerals ground to pass 100-mesh sieve (150 μ).

† Reported in previous paper (5).

TABLE 9
Phosphoric acid (H₃PO₄) fixed by iron minerals

MINERAL		FE IN MINERAL	H ₃ PO ₄ FI-ED PER 100 GM. Fe
		per cent	gm.
Magnetite.....	Fe ₃ O ₄	72.5	0.00
Hematite No. 1.....	Fe ₂ O ₃	69.5	1.64
Hematite R.O.....	Fe ₂ O ₃	69.5	0.11
Limonite.....	2Fe ₂ O ₃ ·3H ₂ O	59.7	1.34
Ilmenite.....	FeO·TiO ₂	27.9	0.04

made to grind hematite, limonite, and magnetite to much smaller sizes than 100-mesh. It has been found difficult to separate the small particles of these minerals by water sedimentation. The fact that phosphate fixation by muscovite is at a maximum near pH 3.5 is of great interest, showing that the aluminum of this mineral is probably active. Gaarder (2) has shown that the minimum solubility of aluminum phosphate in pure salt solutions occurs near this degree of acidity. Work is now under way by the authors to determine the effect of particle size of the various minerals on phosphate fixation.

CONCLUSIONS

Phosphate fixation in soils is dependent on a number of chemical and physical factors.

The data presented for 100-mesh minerals indicate that the mica groups constitute the chief mineral species responsible for phosphate fixation by particles in the fine sand range.

With 100-mesh minerals, the pH for maximum phosphate fixation was about 3.5, which is far below the pH value at which Ca and Mg are active. This value approximates the value given by Gaarder for minimum solubility of iron and aluminum phosphate, indicating that iron and aluminum probably are important in phosphate fixation by these minerals.

No phosphate was fixed by 100-mesh magnetite, but considerable quantities were fixed by limonite and hematite. This shows that the chemical form in which the iron oxide exists in the soil is of great importance in phosphate fixation.

From the literature, it is apparent that the particle size, or surface area presented by the iron oxides, is a major factor in phosphate fixation in soils.

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BOOKS

Conservation in the United States. Second Edition. By A. F. GUSTAFSON, C. H. GUISE, W. J. HAMILTON, JR., AND H. RIES. Comstock Publishing Company, Inc., Ithaca, New York, 1944. Pp. 477, figs. 236. Price, \$4.

This book deals with the conservation of soil and water resources, forest, parks, and grazing lands, wildlife, and mineral resources. In the first section the problem is primarily that of wind and water erosion and its control. In the second section, protection against fire and the restoration of forest growth to idle and nonproductive land are stressed. In the third section, suggestions are offered for the preservation of useful fish, reptiles, birds, and other animals. The fourth section deals with mineral reserves and the possibilities of their exhaustion. The book is exceptionally well illustrated, it is easily read, and it contains a wealth of material, which the student of conservation will find both interesting and useful. It supplements nicely Van Hise's "The Conservation of the Natural Resources in the United States," the pioneer volume in this field of study.

The Field Seed Industry in the United States. By FRANK B. BECK. The University of Wisconsin Press, Madison, 1944. Pp. 230, figs. 49. Price, \$3.

Prepared by the economist of the Field Seed Institute of North America, the book presents a record of the wholesale and retail prices of the more important field seeds, shows graphically the areas of production, presents an index of the relation between production and consumption, state by state, gives data on carry-over in relation to prices, and includes a description of seed-marketing practices. The first chapter is an interesting account of the beginnings of the grass seed industry during early colonial times. The appendix contains 43 pages of tabular material of special value to all those who are concerned with this industry.

The Peats of New Jersey and Their Utilization, Bulletin 55—Part B. By SELMAN A. WAKSMAN, H. SCHULHOFF, C. A. HICKMAN, T. C. CORDON, AND S. C. STEVENS. Department of Conservation and Development, State of New Jersey, Trenton, 1944. Pp. 278, figs. 42, plates XV. Price, \$1.

Part B of this bulletin gives the results of a careful survey of the peat bogs of New Jersey, including data on the depth of the deposits, nature of the original plants, and the chemical composition of the present material. Some 200,000 acres of true peat were surveyed. Sedge and reed peats, forest peats, and the salt marsh and alluvial peats are distinguished. In its entirety, Bulletin 55, comprising Parts A and B, represents a highly important contribution to our knowledge of this subject, and has permanent value in the literature in this field of study.

Pest Control in the Home Garden. By LOUIS PYENSON. The MacMillan Company, New York, 1944. Pp. 190, figs. 111. Price, \$2.

The exceptional feature of this very handy book is the quality of the illustrations, which show not only the weapons for defense against insects but photo-

graphic reproductions of many of these pests at their work of destruction. Anyone interested in gardening will find this a highly useful reference book containing complete instructions for the control of each insect in a very concise form.

Proceedings of the Nineteenth Annual Meeting of the National Joint Committee on Fertilizer Application. H. R. Smalley, general secretary. Published and Distributed by the National Fertilizer Association, Washington, D. C., 1944. Pp. 190.

This is a report of a meeting that was held at Cincinnati, Ohio, November 9, 1943. The organizations represented are The American Society of Agricultural Engineers, The American Society of Agronomy, The American Society for Horticultural Science, The Farm Equipment Institute, and The National Fertilizer Association. Evidence of the interest in the subject of fertilizer placement is shown by the attendance record, which gives the names of 169 men who are concerned in one way or another with the problems involved in this field of endeavor. Reports of all the cooperators are recorded in the Proceedings.

The Standardization of Volumetric Solutions. Second Edition. By R. B. BRADSTREET. Chemical Publishing Company, Inc., 1944. Pp. 151. Price, \$3.75.

The author has confined his attention almost entirely to directions for the preparation of standard acid, base, precipitation, and oxidizing solutions and to stock solutions of indicators and supplementary reagents. The necessary equations are recorded in each case, and logarithmic and other tables for use in calculating the data are appended. Many helpful hints are given. The book constitutes a ready reference which every laboratory analyst would be glad to have close at hand.

THE EDITORS.

CARBONIC ACID SOLUBLE PHOSPHORUS AND LIME CONTENT OF IDAHO SOILS IN RELATION TO CROP RESPONSE TO PHOSPHATE FERTILIZATION¹

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Experimental data and observations show that the soils in the irrigated sections of southern Idaho are becoming more and more deficient in available phosphorus. On the basis of past experience there is every reason to believe that the need for readily available phosphate fertilizers will continue to increase. This situation has created a real need for a method of estimating the available phosphorus in these soils.

Attempts to correlate chemically extractable phosphorus from calcareous soils with plant response have not been too successful in the past. Dilute acid extraction (excepting carbonic acid) is not adaptable to many western soils because of their calcium carbonate content. Solutions buffered with salts such as ammonium or sodium acetate have not been satisfactory because of the dissolving power of the salt regardless of pH. These solutions will extract large quantities of phosphorus from calcareous soils, but the results do not show a significant correlation with crop response. McGeorge (3) used carbonic acid extraction for Arizona soils because this acid was the weakest one adaptable, and because it simulated the mechanism employed by plants in extracting phosphorus from the soil. McGeorge and Breazeale (1) stated that the infertility of certain irrigated soils in Arizona was caused by a deficiency of soluble phosphorus which correlated with such soil properties as water penetration, bacterial activity, and carbon dioxide production. The carbon dioxide producing power of a soil depends mainly on the amount and nature of the soil organic matter present and the evolution of the gas by the roots of growing plants. Workers at the Idaho Station have observed that there is less phosphate deficiency on land that has received liberal applications of crop residues and stable manure than on land untreated with organic matter.

McGeorge and Breazeale (1) concluded that the solvent action of carbonic acid on soil phosphates in calcareous soils is mainly a function of soil reaction. Whitney and Gardner (8) have studied the effect of carbon dioxide on soil reaction. They found that the greatest reduction in pH by carbon dioxide occurred at pressures of less than 0.03 of an atmosphere, whereas pressures above 0.03 of an atmosphere caused only a gradual decrease in pH. Their data

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show that a pressure of one atmosphere reduced the pH value of calcareous soils to slightly above 6 and reduced the pH of noncalcareous soils to a value below 6.

MATERIALS AND METHODS

Numerous phosphate fertilizer tests have been conducted in the irrigated areas of Idaho during the last 6 years under the supervision of the Agricultural Extension Division. Before fertilization and yield data were obtained, soil samples were collected from the untreated and the phosphate-treated plots. Several kinds of phosphate fertilizers were tested, but only the data from plots receiving 125 to 150 pounds per acre of western treble superphosphate or TVA triple superphosphate were used in this study. Likewise, several crops were tested, but this study was limited to tests with alfalfa, sugar beets, and potatoes. The percentage increase in yield due to phosphate fertilization was taken as an indication of the degree to which natural and residual soil phosphates were available to the plant. For the purpose of correlating crop response with carbonic acid soluble phosphorus and lime content of the soil, the following four

TABLE 1

Relationship between response categories and increased yield of various crops when fertilized with phosphate

RESPONSE CATEGORIES	INCREASE IN YIELD DUE TO PHOSPHATE FERTILIZATION		
	Alfalfa	Beets	Potatoes
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
None.....	0-<10	0-<2.5	0-<2.5
Low.....	10-<20	2.5-<10	2.5-<10
Medium.....	20-<45	10-<20	10-<20
High.....	>45	>20	>20

arbitrary response categories were established: none, low, medium, and high. The relationship between the response categories and the percentage increase in yield for the aforementioned crops is presented in table 1.

The carbonic acid extraction was made in the following manner. Ten grams of air-dry soil was placed in a wide-mouthed bottle containing 100 ml. of distilled water. Carbon dioxide was then bubbled through the suspension, with occasional shaking, for 20 minutes. The suspension was filtered and phosphorus determined colorimetrically on an aliquot, a Cenco photometer being used. This method is similar to the one described by McGeorge (3) with the exception that he used a soil-water ratio of 1:5 in place of 1:10.

The lime content was determined by treating a soil sample of known weight with approximately *N* HCl and absorbing the evolved carbon dioxide in standard NaOH. Barium chloride was added to the NaOH, and the excess NaOH titrated with standard HCl, phenolphthalein being used as an indicator. The results were calculated as percentage CaCO₃ and will be referred to later in the paper as "percentage lime."

Soil samples for which crop response data had been obtained were analyzed for carbonic acid soluble P_2O_5 and lime content. Results presented in tables 2, 3, and 4 were analyzed statistically to determine the level of significance between means (5).

RESULTS AND DISCUSSION

The mean P_2O_5 values of the phosphate response categories are given in table 2. The difference between the means of the medium and low response categories is highly significant. There is no significant difference between the means of the medium and high response categories or between the means of the low and no response categories. The difference between the mean P_2O_5 values of the combined medium and high response categories and the combined low and no response categories is highly significant.

There has been much discussion the last few years concerning the relationship between the free lime content of soils and the crop response to phosphate ferti-

TABLE 2
Carbonic acid soluble P_2O_5 in relation to crop response to phosphate fertilization

RESPONSE CATEGORIES	NUMBER OF SAMPLES	MEAN VALUE OF SOLUBLE P_2O_5	DIFFERENCE BETWEEN TWO MEANS OF SOLUBLE P_2O_5
		lbs.	lbs.
High.....	20	9.83	1.92
Medium.....	25	11.75	7.75**
Low.....	21	19.50	2.00
None.....	28	21.50	
High plus medium.....	45	10.93	9.75**
Low plus none.....	49	20.68	

** Significant at the 1 per cent point.

lization. McGeorge (3) reported that $CaCO_3$ reduces the availability and absorption of phosphate because it furnishes calcium ions and affects the soil reaction. Toeve and Baker (6) pointed out that the higher the lime content, the greater the need for phosphate fertilization. Salter and Barnes (4) reported that the long-time field experiments at Wooster, Ohio, showed a notable tendency for phosphate response to decline as the soil reaction was changed from about pH 5.0 to about pH 7.5 by repeated lime applications. They also reported data from a short-time legume-reaction experiment in which crop response to superphosphate was tested at five reaction levels ranging from pH 4.5 to 7.5. With most crops very nearly maximum yields were obtained at the highest reaction level without phosphate. They concluded that satisfactory yields of crops could be produced with the minimum investment in phosphate fertilizers by maintaining the reaction at about pH 7.5. Truog (7), in discussing phosphate availability, pointed out that soils with a pH of 6.5 or above but containing less than 2 per cent calcium carbonate usually contain the greatest amount of

available phosphorus, but at pH 8.0 and above in the presence of 2 per cent or more of calcium carbonate the availability of phosphorus may be lowered in some cases to less than that of basic iron phosphate.

The relationship between lime content and crop response is presented in table 3. Soils falling in the arbitrarily selected 0.5–<1.0 per cent lime range show the lowest response to phosphate fertilization, and the difference between the mean response of these soils and that of the soils in the 1.0–<2.0 per cent lime range is highly significant. Beyond the 1.0–<2.0 per cent lime range there is no appreciable change in response with increasing lime content. The exact lime content above which response is rather high is not apparent because of an insufficient number of samples, but it appears to be very close to 1.0 per cent. Soils containing <0.01 per cent lime show a significantly higher response than soils containing 0.01–<1.0 per cent lime. The relationship between lime content

TABLE 3
Lime content of soils in relation to crop response to phosphate fertilization

LIME	NUMBER OF SAMPLES	MEAN VALUE OF RESPONSE†	DIFFERENCE BETWEEN MEANS OF RESPONSE
<i>per cent</i>			
0	34	2.76	
0.01–<0.50	25	2.08	0.68*
0.50–<1.0	18	1.78	0.30
1.0–<2.0	19	2.74	0.96**
2.0–<4.0	13	2.85	0.09
>4.0	26	2.85	0

† Response categories were given the following numerical values: high = 4, medium = 3, low = 2, and none = 1.

* Significant at 5 per cent point.

** Significant at 1 per cent point.

Note: The mean of the 1.0–<2.0 per cent and the means of all ranges above it are also significantly higher than the mean of the 0.5–<1.0 or the 0.01–<0.5 per cent range.

and soluble P_2O_5 (table 4) is in accord with the relationship between lime and crop response, that is, soluble P_2O_5 is highest in the lime ranges which show the lowest response, and *vice versa*. Also, beyond the 1.0–<2.0 per cent lime range there is no appreciable change in soluble P_2O_5 with increasing lime content.

In analyzing a soil to determine its probable response to phosphate fertilization, therefore, both carbonic acid soluble P_2O_5 and lime content should be determined. These two determinations plus a knowledge of the field conditions should give a fairly reliable indication of the probable crop response to phosphate fertilization. According to the data presented, a soil containing less than 16 pounds per acre of carbonic acid soluble P_2O_5 and more than 1.0 per cent lime would very likely give a medium or high response. Soils containing more than 16 pounds per acre of soluble P_2O_5 and 0.01–<1.0 per cent lime would very likely give a low response or none. Soils which do not contain free lime show a medium response but contain slightly more than 16 pounds per acre of soluble P_2O_5 . In

this case a medium amount of phosphate fertilizer should be recommended, since these soils are not significantly lower in soluble P_2O_5 but do show a significantly higher response than the soils with 0.01–<1.0 per cent lime. Soils that have more than 25 pounds per acre of soluble P_2O_5 seldom respond to phosphate fertilization. Obviously the foregoing procedure for estimating probable crop response is not completely satisfactory, but the authors have found it very helpful in making phosphate fertilizer recommendations for the irrigated soils of Idaho.

The relationship between lime content and crop response may be partly explained on the basis of soil reaction. As would be expected, the soils containing no free lime have a lower average pH than soils containing lime. McGeorge and Breazeale (2) found that iron and aluminum hydroxides in calcareous soils cause considerable phosphate fixation. The fact that the reaction of these soils is more favorable for phosphate fixation by iron and aluminum than the reaction of soils containing a small amount of lime may account

TABLE 4
Carbonic acid soluble P_2O_5 of soils in relation to lime content

LIME	NUMBER OF SAMPLES	MEAN VALUE OF P_2O_5 PER ACRE	DIFFERENCE BETWEEN MEANS
<i>per cent</i>		<i>lbs.</i>	<i>lbs.</i>
0	75	17.58	1.85
0.01–<0.50	35	19.43	2.41
0.5–<1.0	19	21.84	9.90**
1.0–<2.0	17	11.94	0.88
2.0–<4.0	26	12.82	0.22
>4.0	51	13.04	

** Significant at 1 per cent point.

Note: The mean of the 1.0–<2.0 per cent range and the means of all ranges above it are also significantly lower than the means of all ranges below 0.5–<1.0 per cent.

for the significantly higher response of these soils as compared to those having 0.01–<1.0 per cent lime. Soils with more than 1.0 per cent lime have an average pH value of about 8.25. According to McGeorge and Breazeale (1) and Truog (7) a pH of 8.25 would fall in the reaction range of lowest solubility for calcium phosphates. Soils containing 0.01–<1.0 per cent lime have an average pH of approximately 7.75, which is too high for very much iron and aluminum fixation but not high enough to fall in the reaction range of lowest calcium phosphate solubility.

According to the data in table 2 approximately 50 per cent of the soils show a medium or high response to phosphate fertilization. Three hundred soil samples taken at random from the same general area were analyzed for carbonic acid soluble P_2O_5 . Approximately 50 per cent of the soils contained less than 16 pounds per acre of soluble P_2O_5 , which would indicate a probable medium or high response. These data indicate a rather widespread phosphate deficiency and emphasize the importance of phosphate availability studies on these soils.

CONCLUSIONS

Soil samples of known crop response to phosphate fertilization were analyzed for carbonic acid soluble phosphorus and lime content for the purpose of correlating results thus obtained with crop response. To aid in the correlation the following four arbitrary degrees of response categories were established: none, low, medium, and high.

The difference between the mean P_2O_5 values of the combined medium and high response categories and the combined low and no response categories was highly significant. Soils in the medium response category were significantly higher in soluble P_2O_5 than soils in the low response category. There was no significant difference between the means of the high and medium response categories or between the means of the low and no response categories.

Soils containing 0.5–<1.0 per cent lime showed the lowest response to phosphate fertilization, and the mean response of these soils as compared to the mean response of the soils in the 1.0–<2.0 per cent lime range was highly significant. Beyond the 1.0–<2.0 per cent lime range there was no appreciable change in response with increasing lime content. Soils containing less than 0.01 per cent lime gave as great a response as soils containing more than 1.0 per cent lime. Carbonic acid soluble P_2O_5 was highest in the lime ranges which showed the lowest response, and *vice versa*. Also, there was no significant change in soluble P_2O_5 with increasing lime content in the lime ranges greater than 1.0–<2.0 per cent.

The data presented show that approximately one half of the soils of the irrigated areas of southern Idaho gave a medium or high response to phosphate fertilization.

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AIR AND SOIL TEMPERATURES IN A CALIFORNIA CITRUS ORCHARD¹

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Air temperatures in the citrus-growing districts of California have received considerable attention because of the possibility of frost injury to fruit and trees during the winter months. Little is known about soil temperatures, however, especially those of the southern coastal region, where the principal plantings of oranges and lemons are situated. Girton (4) observed growth in citrus roots at temperatures between 55.4° and 98.6° F., the most rapid elongation occurring at 80.6°. Fawcett (3) reported a similar range of temperatures to be favorable to the germination of citrus seeds. Webber (9), in a recent discussion of the growth and temperature relations of citrus, pointed out that "soil temperatures at a one-foot depth at Riverside, California, ordinarily do not go above 55° F. during February. They continue cool throughout March, ranging commonly between 50° F. and 65° F. but remaining for extended periods approximately at 55° F. Under such conditions root growth would be expected to remain inactive, at least until the latter part of March, as it apparently does. . . ."

In connection with an investigation of the armillaria root rot of citrus, air and soil temperatures have been carefully studied in a Valencia-orange orchard in the coastal region near Anaheim, California. Data obtained without interruption from February, 1939, to July, 1943, appear to be of sufficient importance to warrant separate publication. A similar study of air and soil temperatures in a date garden in the inland region near Indio, California, was reported in 1942 by Bliss, Moore, and Bream (1). These two studies have revealed certain differences in the relation of air and soil temperatures at Indio and at Anaheim. Underlying reasons for these differences are discussed.

TEMPERATURE READINGS

The temperature data for the present study were obtained in an orchard of mature Valencia-orange trees situated 1½ miles west of Anaheim, California, on the broad flood plain of the Santa Ana River. In this locality irrigation is necessary in summer because precipitation is low (about 12 inches annually) and occurs mostly from November to April. Situated at an elevation of about 160 feet and at a distance of 10 miles from the coast line, the orchard is subject to the prevailing cool ocean breezes from the southwest, and to occasional hot, dry

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² Associate plant pathologist in the experiment station. The author is indebted to Herman H. Freese, in whose orchard these data were obtained, and who recorded the temperatures, and also to H. E. Wahlberg, Robert O. Bream, Newton Noble, Carl Moore, George Jeffrey, Elizabeth Parker, and L. C. Masters for their cooperation and assistance.

winds arising in the interior desert regions to the northeast. The soil is classified as Hanford sandy loam (2); its texture at different depths is shown in table 1.

The vertical distribution of citrus roots in this soil is indicated by the data presented in table 2. Roots from an excavation 30 inches wide, 57 inches long, and 52 inches deep, in soil that had not been disturbed for more than 4 years, near the "drip" of a tree in close proximity to the temperature instruments, were measured and weighed. None of the taproots or larger lateral roots were encountered. Slightly more than half of the roots (by weight) were found in the upper 18 inches of soil; a few extended to a depth of 52 inches (table 2).

TABLE 1

*Texture and moisture content of Hanford sandy loam at site of temperature instruments in orchard at Anaheim, California**

DEPTH	TEXTURE	MOISTURE CONTENT
<i>feet</i>		<i>per cent</i>
0-1	Sandy loam	18.5
1-2	Coarse sandy loam	12.8
2-3	Coarse sandy loam	13.6
3-4	Loamy sand	20.6
4-5	Sandy loam (upper 9 inches), clay	15.5
5-6	Clay (upper 2 inches), sand	10.5
6-7	Sharp sand	4.1
7-8	Sharp sand	2.6
8-9	Sharp sand	2.5

* Determinations made by Martin R. Huberty, February 14, 1939.

TABLE 2

Vertical distribution of roots of orange tree in soil near temperature instruments

DEPTH	DIAMETER OF LARGEST ROOT	ROOTS, DRY-WEIGHT BASIS	
<i>inches</i>	<i>mm.</i>	<i>gm.</i>	<i>per cent</i>
0-6	6.5	33.20	10.72
6-18	12.9	124.90	40.32
18-30	7.6	104.71	33.80
30-42	6.1	41.05	13.25
42-52	3.2	5.90	1.91

The site chosen for this study was near the center of a 5-acre block of Valencia-orange trees, bordered on the west, north, and east by windbreaks of eucalyptus trees. A carefully leveled rectangular area, 24 by 48 inches, near the southeast side of a tree, was selected for the installation of the instruments (fig. 1). On clear days this area was normally exposed to the sun from early morning to mid-afternoon. A low wire fence excluded small animals from the area. The surface of the soil was kept free from weeds and cover crop during the period of the temperature readings; irrigation water was permitted to cover the entire area.

An air thermograph and maximum-minimum thermometers were installed 5

feet above the ground in the upper room of an instrument shelter (fig. 1). The instrument heads of two dual soil thermographs were placed in two lower rooms. Three of the grid-type bulbs of these thermographs were buried in the soil of the unshaded, fenced area on the south side of the shelter, at depths of 3, 6, and 12 inches, respectively; the fourth bulb was buried 3 inches deep in shaded soil near the trunk of the tree. The bulbs were inserted in a horizontal position

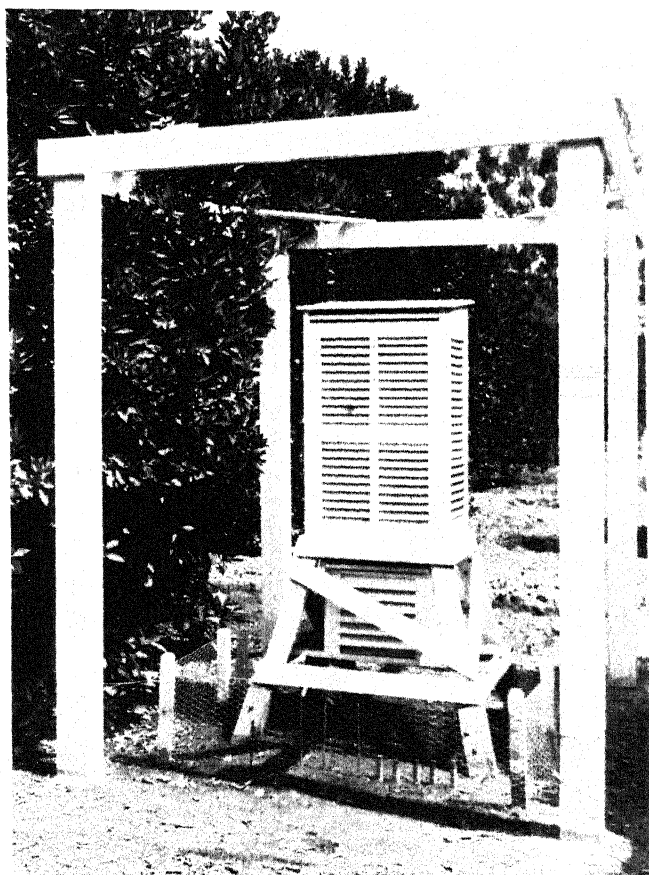


FIG. 1. INSTRUMENT SHELTER AND SMALL FENCED ENCLOSURE IN VALENCIA-ORANGE ORCHARD NEAR ANAHEIM, CALIFORNIA, WHERE AIR AND SOIL TEMPERATURES WERE STUDIED

into niches in the side of a shallow trench and were centered at the desired depths, care being taken to disturb the soil as little as possible. Soil from each niche was returned and packed firmly about the grids. A mercury thermometer encased in metal armor was inserted in the soil beside each of the four thermograph bulbs for the purpose of checking, each week, the accuracy of the thermograph readings. These thermometers, and also one with its bulb inserted 24

inches below the surface, were of the emersion type. In each case the upper end of the mercury column could be read on the scale without lifting the thermometer.

For measurement of the temperatures of unshaded soil at depths of 2, 3, 4, 6, and 8 feet, respectively, standard thermometers encased in metal armor were lowered by means of copper wires into bakelite pipes. The pipes had been inserted in vertical holes made by driving a soil tube into the soil to the different desired depths. The bulbs of the thermometers, except the lower end, which touched the soil, were wrapped with asbestos and adhesive tape to prevent cooling by the evaporation of moisture when the thermometers were raised to the surface for reading. The exposed ends of the pipes protruded 3 inches above the ground and were kept tightly closed with rubber stoppers to which the copper wires were attached. Readings were made on these standard thermometers once each week (table 3) at the time when the thermograph charts were changed.

Weekly mean temperatures of the air and of the soil (table 3) at 3-, 6-, and 12-inch depths in unshaded soil, and at a 3-inch depth in shaded soil, were calculated from the thermograph charts by means of a polar planimeter. The method was the same as that described by Bliss, Moore, and Bream (1). Corrections were made on the weekly mean temperatures of the air and of the soil at 3- to 24-inch depths. Soil temperatures at 3- to 8-foot depths could be checked during the study only by inspection and comparison. At the close of the study, however, all the standard thermometers were tested at five different temperature levels and were found to agree within 0.5° F. with a certified thermometer. Other precautions included the use of uniform bakelite pipes (a material having low heat conductivity) and the burying of the thermograph capillary tubes at the same depths as the bulbs. With few exceptions, the thermometers were read and the charts changed regularly each Monday at 7:00 a.m.³ Two of the thermograph bulbs had to be taken up temporarily for repair, but the instruments were generally very accurate, and considerable confidence is expressed in the data obtained.

Although the data are summarized principally as weekly mean temperatures (table 3), additional information on the yearly range of air and soil temperatures, 1939-1942, is given (table 4). Whereas in this period the minimum air temperatures were 27° to 32° F., the maximum air temperatures ranged from 93° to 111° . The yearly range of recorded temperatures in the unshaded soil was greatest at a depth of 3 inches and least at 8 feet. The yearly ranges of temperature for the different depths, considered separately, were remarkably uniform, especially those at the lower levels. The maximum temperatures at the 3-inch depth were more than 20 degrees cooler in shaded soil than in unshaded soil.

Various meteorological conditions were associated with wide variations in the range of daily temperature fluctuations in the air and in soil near the surface during this study. Hourly temperature readings of air and of unshaded soil at depths of 3, 6, and 12 inches, respectively, were transcribed from certain

³ Pacific Standard Time.

TABLE 3

Weekly mean temperatures of air and soil* in a Valencia-orange orchard at Anaheim, California, February, 1939, to July, 1943

DATE, WEEK ENDING:	TEMPERATURE OF AIR	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS									
		Shaded	Unshaded								
			3 inches	3 inches	6 inches	1 foot	2 feet	3 feet	4 feet	6 feet	8 feet
°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.		

1939										
Feb. 20	48			51	52	51	52	53	54	56
27	49			53	53	53	52	53	54	56
Mar. 6	46			49	51	51	52	53	54	56
13	47			53	54	54	53	53	54	56
20	53			56	55	55	55	54	54	56
27	52			56	56	55	55	55	55	56
Apr. 3	55			58	58	58	57	56	56	56
10	60			65	63	62	60	58	56	57
17	54			64	64	61	60	59	58	57
24	58			66	65	63	62	60	59	58
May 1	57			64	64	64	62	61	60	59
8	58			66	66	65	63	61	60	59
15	60			65	66	64	63	62	61	60
22	60			65	65	65	63	62	61	60
29	64			70	69	68	65	63	62	61
June 5	63			70	70	68	67	65	63	61
12	65			..†	67	67	66	65	64	62
19	62			67	68	67	66	65	64	62
26	64			69	69	68	67	66	64	63
July 3	68			71	71	71	69	67	65	63
10	66			73	73	72	70	68	66	64
17	70			75	75	73	71	69	66	65
24	68			73	73	71	71	70	67	66
31	..			71	71	70	70	69	67	65
Aug. 7	70			74	73	73	71	70	68	66
14	66			74	74	73	71	70	68	66
21	68			76	75	75	72	70	68	66
28	70			77	77	74	73	71	69	67
Sept. 4	68			72	73	72	72	71	69	67
11	70			74	73	74	71	70	69	67
18	69			75	74	74	72	70	69	68
25	84			85	82	78	75	72	70	68
Oct. 2	63			71	72	72	71	71	70	68
9	58			67	71	67	69	69	69	68
16	66			70	69	69	68	68	68	67
23	64			70	69	69	68	68	67	67
30	58			66	67	66	66	67	67	67

TABLE 3—Continued

DATE, WEEK ENDING:	TEMPERA- TURE OF AIR	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS									
		Shaded	Unshaded								
			3 inches	3 inches	6 inches	1 foot	2 feet	3 feet	4 feet	6 feet	8 feet
1939—Continued											
Nov. 6	60			66	65‡	65	65	66	66	66	
13	56			64	63‡	63	64	65	65	66	
20	56			60	60‡	61	63	64	65	65	
27	58			60	59	61	62	62	64	64	
Dec. 4	56			58	58‡	59	61	62	63	64	
11	58			58	59‡	60	60	61	62	63	
18	54			56	58‡	57	59	60	62	63	
25	48			54	54‡	54	57	59	61	62	
1940											
Jan. 1	50			52	53‡	55	56	57	59	61	
8	52			54	55‡	56	57	57	59	61	
15	54			56	54‡	56	57	58	59	60	
22	48			52	52‡	53	55	57	59	60	
29	54			54	54‡	55	55	56	58	60	
Feb. 5	54			58	55‡	56	56	57	57	59	
12	50			56	54‡	56	56	57	58	59	
19	48			54	52‡	55	55	56	57	59	
26	56			56	57	57	56	56	57	59	
Mar. 4	56			60	55	58	58	57	57	59	
11	54			60	59	58	58	58	58	59	
18	54			60	59	59	58	58	58	59	
25	56			60	61	59	59	58	58	59	
Apr. 1	58			62	61	60	59	59	59	59	
8	54			60	61	60	60	59	59	59	
15	66			67	65	65	..	60	59	59	
22	58			67	66	65	63	61	60	60	
29	56			63	64	62	62	62	61	60	
May 6	62			67	65	65	63	62	61	61	
13	64			71	68	68	65	63	62	61	
20	63	61	73	72	70	69	67	65	63	62	
27	64	63	71	71	69	69	67	66	64	63	
June 3	64	62	72	71	70	70	68	66	65	63	
10	63	63	69	69	69	67	67	66	65	64	
17	64	63	68	68	67	67	67	66	65	64	
24	64	63	67	67	67	68	67	66	65	64	
July 1	64	63	70	70	69	70	68	67	65	65	
8	66	65	74	73	72	72	70	68	66	65	
15	71	67	78	76	76	74	71	69	67	65	
22	64	64	77	74	74	73	71	70	68	66	
29	67	67	75	74	74	71	71	70	68	66	

TABLE 3—Continued

DATE, WEEK ENDING:	TEMPERA- TURE OF AIR	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS								
		Shaded	Unshaded							
			3 inches	3 inches	6 inches	1 foot	2 feet	3 feet	4 feet	6 feet
		°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.
1940—Continued										
Aug. 5	67	67	74	73	72	72	70	69	68	67
12	70	68	79	77	76	75	72	70	69	67
19	67	66	76	77	75	74	72	71	69	67
26	67	66	78	79	76	75	73	71	70	68
Sept. 2	66	66	76	78	75	73	72	71	70	68
9	66	65	72	72	72	71	71	71	70	68
16	65	65	73	73	72	72	71	70	69	68
23	64	64	73	74	72	72	71	70	69	68
30	65	64	77	76	74	73	71	70	69	68
Oct. 7	61	62	73	72	72	71	70	70	69	68
14	63	63	69	70	69	68	68	68	68	68
21	66	64	70	69	69	68	68	68	68	67
28	60	63	65	68	68	65	66	67	67	67
Nov. 4	56	57	61	62	63	63	64	65	66	66
11	55	56	59	59	60	60	62	63	65	65
18	59	58	56	58	59	59	61	62	64	65
25	48	51	52	54	55	55	58	60	62	64
Dec. 2	53	51	53	53	54	55	57	59	61	63
9	54	53	55	55	55	55	57	58	60	62
16	54	52	55	55	56	55	57	58	60	61
23	53	53	56	55	55	56	57	58	59	61
30	50	53	54	54	55	55	56	57	59	60
1941										
Jan. 6	48	51	52	52	53	53	55	56	58	60
13	51	52	54	54	54	54	55	56	58	60
20	49	50	52	52	53	53	55	56	57	59
27	51	52	53	53	53	54	55	55	57	59
Feb. 3	54	53	57	56	56	56	56	56	57	58
10	54	53	57	56	56	56	56	56	57	58
17	51	54	58	57	57	56	56	56	57	58
24	55	56	60	60	58	58	57	57	57	58
Mar. 3	53	55	59	60	59	58	58	58	58	59
10	56	55	61	61	60	59	58	58	58	59
17	57	57	62	63	62	60	59	59	58	59
24	55	57	62	63	62	60	59	59	59	59
31	57	58	64	65	63	61	60	..	59	59
Apr. 7	53	56	51	62	61	60	60	60	59	59
14	53	56	60	60	61	59	60	60	60	60
21	52	54	60	61	60	60	60	60	60	60
28	62	58	64	64	62	62	61	60	60	60

TABLE 3—Continued

DATE, WEEK ENDING:	TEMPERA- TURE OF AIR	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS								
		Shaded	Unshaded							
			3 inches	6 inches	1 foot	2 feet	3 feet	4 feet	6 feet	8 feet
			°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.

1941—Continued

May 5	56	58	63	62	61	62	61	61	60	60
12	68	65	73	70	68	67	64	62	61	60
19	60	61	69	68	67	66	65	64	62	61
26	66	62	73	73	71	69	67	65	63	62
June 2	62	63	71	70	67	69	67	66	64	62
9	60	63	69	70	69	68	67	66	65	63
16	64	63	72	72	71	69	68	67	65	..
23	64	65	74	74	73	72	70	68	66	..
30	61	63	66	68	68	68	68	68	67	65
July 7	64	64	69	69	67	70	68	67	66	65
14	66	66	73	73	71	71	70	68	67	65
21	67	67	78	77	74	75	71	70	67	66
28	66	67	76	76	74	74	72	70	68	66
Aug. 4	67	66	75	76	74	73	72	71	69	67
11	66	67	71	73	71	71	71	70	69	67
18	69	69	75	76	73	74	71	70	69	67
25	67	68	78	79	77	75	73	71	69	67
Sept. 1	64	65	72	73	73	73	72	71	70	68
8	65	66	74	76	74	72	72	71	69	68
15	63	65	69	73	71	70	70	70	69	68
22	61	62	68	69	69	69	69	69	69	68
29	59	59	72	72	69	70	69	69	68	67
Oct. 6	64	59	73	72	72	71	70	69	68	67
13	60	61	73	72	71	70	69	68	68	67
20	62	62	71	71	70	69	69	68	67	67
27	53	58	60	61	62	63	64	65	66	66
Nov. 3	55	56	60	60	60	62	63	64	65	66
10	60	60	63	64	62	63	63	63	64	65
17	58	59	62	62	60	62	62	63	64	64
24	48	50	52	53	57	56	59	61	63	64
Dec. 1	53	52	..	54	55	56	58	59	61	63
8	50	53	..	54	55	55	57	59	60	62
15	51	53	..	53	54	55	56	58	60	61
22	50	53	..	54	55	55	56	57	59	61
29	44	47	..	47	48	51	53	56	58	60

1942

Jan. 5	40	46	..	47	49	50	52	55	57	60
12	53	..	54	50	50	52	53	54	56	59
19	53	..	54	54	53	53	54	54	56	58
26	55	..	54	55	54	54	54	55	56	58

TABLE 3—Continued

DATE, WEEK ENDING:	TEMPERATURE OF AIR	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS									
		Shaded	Unshaded								
			3 inches	3 inches	6 inches	1 foot	2 feet	3 feet	4 feet	6 feet	8 feet
*F.	*F.	*F.	*F.	*F.	*F.	*F.	*F.	*F.	*F.		
1942—Continued											
Feb. 2	51	..	54	54	55	54	54	55	56	58	
9	52	..	56	54	53	55	55	55	56	58	
16	47	..	52	53	54	52	54	55	56	58	
23	47	..	53	53	53	53	53	54	55	57	
Mar. 2	49	..	54	54	54	54	54	54	55	57	
9	52	..	60	59	58	57	55	55	55	57	
16	51	..	58	58	58	55	56	56	56	57	
23	51	..	60	59	58	57	56	56	56	57	
30	52	..	64	62	61	60	57	56	56	57	
Apr. 6	57	..	65	63	62	60	59	58	57	58	
13	56	..	61	60	60	59	58	58	57	58	
20	55	..	62	62	60	60	59	58	58	58	
27	53	..	64	61	61	60	59	59	58	58	
May 4	53	..	61	61	60	59	59	59	58	59	
11	58	..	63	64	62	61	60	59	59	59	
18	55	..	63	62	62	62	61	60	59	59	
25	63	..	70	70	68	66	64	62	60	60	
June 1	59	..	69	69	68	68	65	63	61	60	
9	61	..	70	70	67	68	66	64	62	61	
17	63	..	66	67	67	66	65	64	63	62	
22	61	..	67	67	66	66	65	64	63	62	
29	63	..	71	71	70	68	67	65	64	62	
July 6	65	..	71	71	70	70	68	66	65	63	
13	68	..	78	75	74	73	70	68	65	64	
20	68	..	79	78	77	75	72	69	67	64	
27	68	..	75	75	74	72	71	70	68	65	
Aug. 3	64	..	74	72	71	72	70	70	67	66	
10	67	69	78	77	74	73	71	70	68	66	
17	68	68	78	78	76	74	72	70	69	68	
24	69	69	81	82	78	75	73	71	69	67	
31	64	66	78	78	77	74	73	71	69	67	
Sept. 7	58	63	69	70	69	69	69	70	69	67	
14	62	64	70	71	70	70	69	69	68	67	
21	64	64	74	74	73	71	70	69	68	67	
28	65	66	76	76	74	71	70	69	68	67	
Oct. 5	64	64	72	73	71	71	70	69	68	67	
12	63	64	71	72	71	70	70	69	68	67	
19	61	62	70	71	69	69	68	68	67	66	
26	62	64	67	69	68	66	66	67	67	66	

TABLE 3—Continued

DATE, WEEK ENDING:	TEMPERA- TURE OF AIR	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS									
		Shaded	Unshaded								
			3 inches	3 inches	6 inches	1 foot	2 feet	3 feet	4 feet	6 feet	8 feet
1942—Continued											
Nov. 2	57	58	61	62	61	62	64	65	66	66	
9	56	58	60	61	61	61	63	63	65	65	
16	58	58	60	61	61	61	62	62	64	65	
23	53	55	56	58	58	58	60	61	63	64	
30	51	54	55	56	56	57	58	60	62	63	
Dec. 7	51	53	53	55	57	56	58	59	61	62	
14	48	50	50	50	52	53	57	57	60	61	
21	52	51	52	52	53	54	55	57	59	61	
28	51	51	52	52	53	53	55	56	58	60	
1943											
Jan. 4	51	51	52	53	53	53	54	55	57	60	
11	49	48	49	51	51	51	53	54	56	59	
18	49	49	50	51	50	52	53	54	56	58	
25	49	50	50	50	51	53	53	54	55	58	
Feb. 1	51	53	54	53	54	54	54	54	55	58	
8	50	51	53	52	53	53	54	54	55	57	
15	55	53	55	54	54	55	54	54	55	57	
22	55	54	57	57	57	56	55	55	55	57	
Mar. 1	50	54	54	55	56	55	55	55	56	57	
8	56	56	58	57	58	57	56	56	56	57	
15	56	56	59	59	60	58	58	57	57	58	
22	53	54	58	59	58	58	58	57	57	58	
29	56	55	61	61	61	60	59	58	57	58	
Apr. 5	57	56	62	63	62	61	60	59	58	58	
12	53	54	59	58	59	59	59	59	58	58	
19	57	57	62	61	59	60	59	59	58	58	
26	58	58	63	64	62	62	61	60	59	59	
May 3	61	59	69	67	65	65	62	61	60	59	
10	61	60	68	68	67	65	63	61	60	60	
17	60	60	72	72	72	66	65	63	61	60	
24	64	62	74	71	69	68	66	64	62	61	
31	62	62	68	68	68	66	65	64	63	61	
June 6	60	61	68	67	67	67	65	64	63	62	
13	60	62	67	68	68	65	65	65	63	62	
20	64	63	68	69	68	67	65	64	63	62	
27	60	64	73	72	70	69	67	65	64	63	
July 5	63	63	73	71	70	69	68	67	65	63	
12	66	65	75	71	69	67	65	64	

* Temperatures of the air and of the soil at depths of 3, 6, and 12 inches were recorded by thermographs, and weekly mean temperatures were calculated from the thermograph charts by means of a planimeter. Temperatures of soil at depths of 2, 3, 4, 6, and 8 feet were determined by weekly readings on standard thermometers.

+ Leaders indicate data lacking.

thermograph charts and combined on graphs with rectangular coordinates. Four periods of 48 hours each are presented to illustrate (a) the warm, clear weather observed each summer for 2 to 6 weeks (fig. 2, A); (b) the hottest and (c) the coldest weather, respectively (fig. 2, B and C); and (d) the cool, cloudy weather observed each winter for 3 to 7 weeks (fig. 2, D).

On August 10, 1940 (fig. 2, A), the air reached its minimum temperature (57° F.) at 4 a.m. and its maximum (91°) at 1 p.m. Complete reversals in the relative value of the soil temperatures occurred about midnight and between 9 and 11 a.m. Minimum soil temperatures occurred from 5 a.m. (at the 12-inch depth) to 7 a.m. (at the 3-inch depth), whereas the maxima were reached between 2 and 3 p.m. Diurnal fluctuation of temperature was greatest in soil at 3 inches and least at 12 inches. Comparison of the extremes of temperature of the air and of the soil at 3 inches, reveals that the soil was 13 degrees warmer than the air at the minima, and 2 degrees warmer at the maxima.

TABLE 4

Yearly range of air and soil temperatures in a Valencia-orange orchard at Anaheim, California, 1939 to 1942, inclusive

YEAR	TEMPERATURE OF AIR*	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS								
		Shaded	Unshaded							
		3 inches	3 inches	6 inches	1 foot	2 feet	3 feet	4 feet	6 feet	8 feet
	°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.
1939†	27-111	43-95	54-86	51-78	52-75	53-72	54-70	56-68
1940	32-100	—74	—97	46-89	52-79	53-75	55-73	56-71	57-70	59-68
1941	27- 93	42-74	41-98	42-89	47-79	51-75	53-73	55-71	57-70	58-68
1942	27- 97	40-96	41-90	46-79	53-75	52-72	54-71	55-69	57-68

* Thermograph 5 feet above the ground.

† First records obtained February 14, 1939.

On September 20, 1939 (fig. 2, B), air temperatures ranged from 67° F. at 1 a.m. to 111° at 1 p.m., while soil temperatures ranged from 77° to 93° at the 6-inch depth and from 78° to 83° at the 12-inch depth. In contrast to this is the period January 1-2, 1942 (fig. 2, C). The air temperature, after reaching 49° at 11 a.m. of the first day, fell to 27° at 6 a.m. of the second day and then rose to 59° at 1 p.m. Soil temperatures on the first day ranged from a maximum of 51° at the 12-inch depth to a minimum of 46° at the 6-inch depth; on the second day, the range was from a minimum of 42° at the 6-inch depth to a maximum of 49° at both depths. The temperatures at the 6-inch depth remained lower than those at 12 inches on both days, except during 4 hours when they were the same. Unfortunately, no record of soil temperatures at 3 inches was obtained in these periods of extreme temperatures.

Relatively small diurnal fluctuations in temperature accompanied rainy weather on January 5, 1941 (fig. 2, D). The range of air temperatures was 40° to 53°F., while that of soil temperatures at 3 inches was 48° to 53°, and at 12 inches, only 51° to 52°.

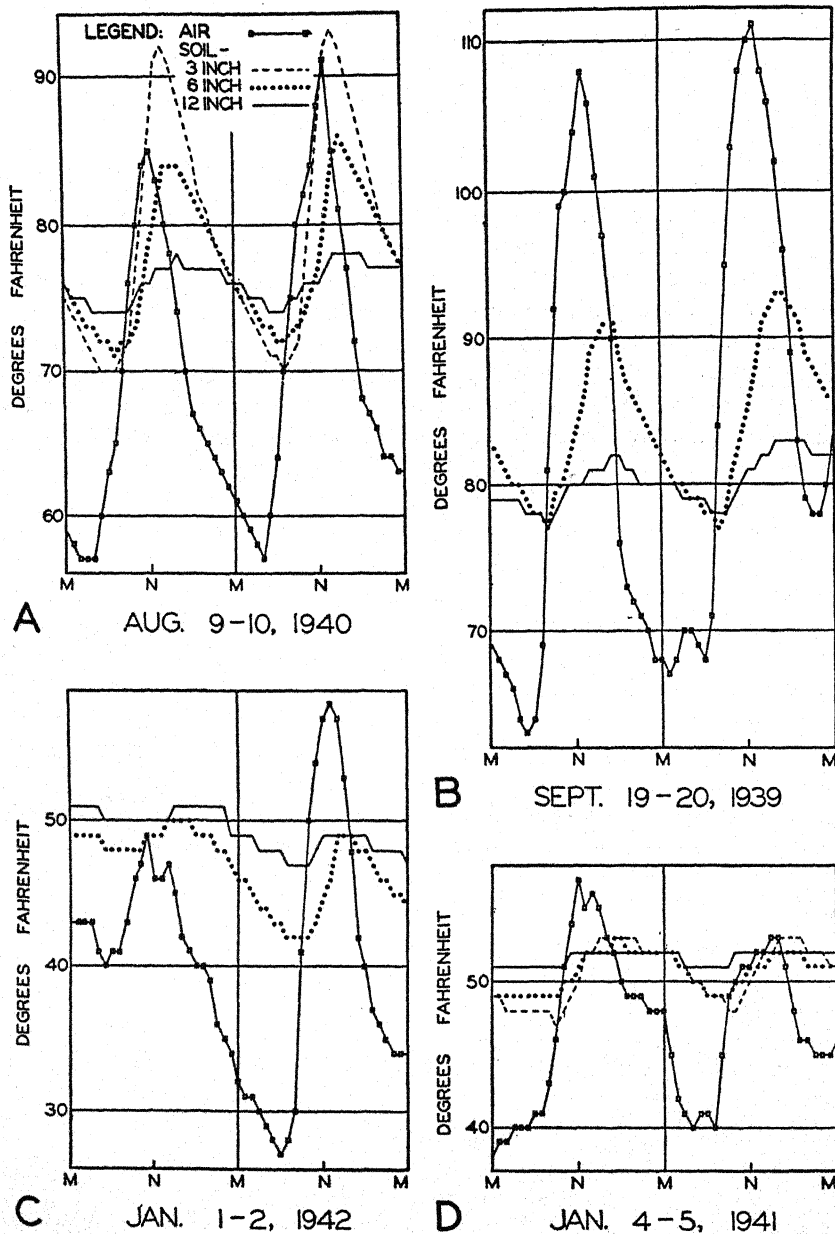


FIG. 2. DIURNAL TEMPERATURE FLUCTUATIONS OF AIR AND OF SOIL AT 3-, 6-, AND 12-INCH DEPTHS, IN VALENCIA-ORANGE ORCHARD AT ANAHEIM, CALIFORNIA, DURING FOUR 48-HOUR PERIODS REPRESENTING DIFFERENT METEOROLOGICAL CONDITIONS
M, midnight; *N*, noon; *A*, warm, clear, summer weather; *B*, the hottest weather encountered; *C*, the coldest weather encountered; *D*, cool, cloudy winter weather.

DISCUSSION

The temperature data presented in this paper contribute to an understanding of the climate at Anaheim, which is in the most important citrus-growing region of California. Judged from the relatively high quality of fruit produced in this locality, the temperature environment is also one of the most favorable for the culture of Valencia oranges in the state. The climate is characterized by relatively mild air temperatures throughout the year. Overturms in the temperature of the soil at different depths occur regularly in spring and fall each year.

There is marked evidence of lag in the time at which the soil at different depths reached the yearly minimum temperatures. When compared with the air-temperature curve, the temperature curve for soil at the 1-foot depth showed a brief lag, and that for the soil at the 8-foot depth lagged for several weeks. The yearly maximum temperatures of air and soil were more or less concurrent.

Marked similarity exists between the weekly mean temperatures of the air and of shaded soil at the 3-inch depth, and also between the weekly mean temperatures of unshaded soil at 3- and 6-inch depths.

In an earlier study of air and soil temperatures at Indio, California (1), the weekly mean temperatures of the air from April to September, inclusive, were typically 5 to 10 degrees higher than those of soil at the 1-foot depth. At Anaheim, however, the weekly mean temperatures of air from April to August, inclusive, fluctuated in the same range as those of soil at 3- to 8-foot depths, and only on rare occasions were they as high as those of soil at the 1-foot depth. This remarkable difference in the relation of air and soil temperatures during the spring and summer months in the two localities is shown by the data for 1936 from Indio (fig. 3) and for 1940 from Anaheim (fig. 4).

In the figures mean weekly temperatures of the air and of the soil at 1- and 6-foot depths are compared. The interrelation of soil temperatures was similar at both stations, but the air temperatures were relatively high at Indio (fig. 3) and low at Anaheim (fig. 4).

This difference between air temperatures at Indio and Anaheim is attributed to the thermal preconditioning of the air at the two stations. Whereas the temperature condition of the soil, measured at a certain point below the surface, is extremely localized, that of the air is not so localized but results from constant movement of air over the earth's surface. Heat exchange undoubtedly occurs where a temperature gradient exists. Air moving over land or water tends to gain or to lose heat according to the temperature of the substratum; thus cool winds passing over hot desert soil become warmed, and warm winds passing over the Pacific Ocean become cooled. A soil-surface temperature of 172° F. and an air temperature of 122° were reported at Indio, California, on July 12, 1934.⁴ McEwen (6) found the mean ocean temperature at La Jolla, California, to be 67.6° for the 10-week interval August 1 to October 15, in the years 1916 to 1922.

⁴ Data supplied by Dewey C. Moore, formerly at the United States Date Garden, Indio, California.

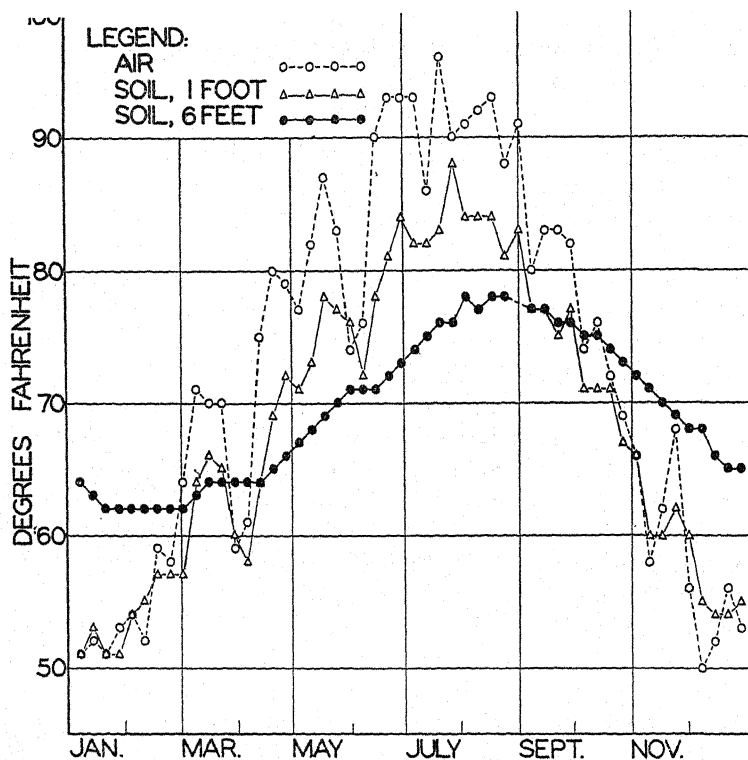
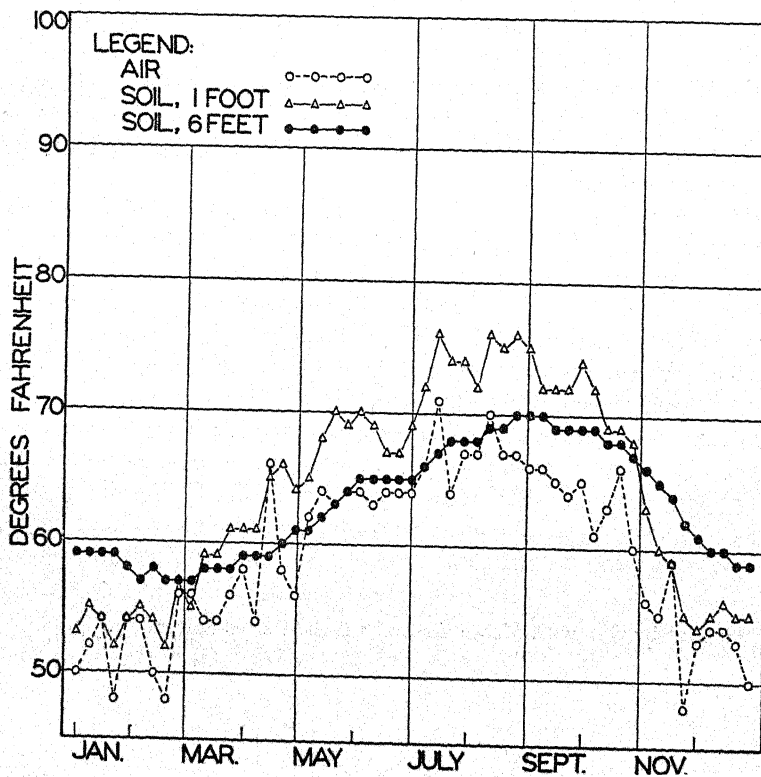


FIG. 3. WEEKLY MEAN TEMPERATURES OF AIR AND SOIL, INDIO, CALIFORNIA, 1936



According to Leighly (5), "the primary effect of a water body on the march of temperature in the air above it depends upon the storage of an appreciable fraction of the heat produced by absorption of the solar radiation that falls on it during the summer, and the liberation of that heat to maintain the temperature of the overlying air in winter."

Sprague (8) states that "the Pacific Ocean, in connection with prevailing westerly winds, gives the immediate coastal area [of California] a true marine climate. The Coast Range, acting as a barrier, nearly nullifies this water influence on its eastern sides, except in areas opposite breaks in the barrier; hence most of the interior has either a continental or a mountain climate. . . . The coastal area is marked by moderate temperatures, with small daily and annual ranges, and freezing weather is infrequent. . . ."

It seems, therefore, that the prevailing southwesterly winds at Anaheim are relatively cool in summer because of their preconditioning over the Pacific Ocean only 10 miles away. The prevailing northwesterly winds at Indio are relatively warm in summer because of their preconditioning over many miles of hot inland valley and desert land. The unusually warm weather at Anaheim in September, 1939, was probably due to the influx of heated air from the desert.

The relation of air and soil temperatures at Davis, California, as reported by Smith (7), is similar to that at Anaheim. Although Davis is situated more than 50 miles from the ocean, the climate there is perhaps affected by marine air blowing inland along the Sacramento Valley.

SUMMARY

Temperatures of air and soil in a Valencia-orange orchard near Anaheim, California, were recorded from February, 1939, to July, 1943. The data are summarized as weekly mean temperatures and as yearly ranges.

Wide variations in the range of daily temperature fluctuations in the air and in the soil near the surface were associated with different meteorological conditions.

The relations of air and soil temperatures in summer at Anaheim and at Indio, California, are discussed. The relatively cool air of the coastal climate at Anaheim is attributed to the thermal preconditioning of the prevailing southwesterly winds over the Pacific Ocean. The relatively warm air of the inland climate at Indio is attributed to the preconditioning of northwesterly winds over many miles of hot interior valley and desert land.

REFERENCES

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PRINCIPLES OF SOIL SAMPLING

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Although sampling error is commonly much greater than analytical error for soils, research upon which sound sampling procedure could be based is very limited. As a result, instructions for sampling abound in statements that proper procedure depends upon the objective. True as such observations are, they contribute little to an investigator faced with a sampling problem. This article is presented in the hope that the general principles of sampling outlined may serve as guides in sampling for many objectives and that research upon which more precise sampling standards can be based will be stimulated.

A value obtained by chemical analysis of soil defines specifically a characteristic of a small subsample. The value approximates an accurate definition of a characteristic of the soil only to the extent that (a) the gross sample accurately represents the soil from which it was taken, (b) no changes affecting the results occur in the sample prior to analysis, (c) the subsample analyzed represents the gross sample accurately, and (d) the analysis determines the true value of the characteristic under test (18). Probable errors three to six times greater for sampling and sample treatment than for subsampling and analysis have been reported for much more precise sampling methods than are commonly employed (27, 33, 34). The limit of accuracy generally is determined by the sample, not by the analysis.

A CONCEPT OF SOIL FOR SAMPLING

Soil volumes, not areas, are sampled. Each volume from which a sample is drawn may be considered a *population* composed of many *individuals*, or primary particles, that vary among themselves both vertically and horizontally (29). It is convenient to treat a group of closely associated primary particles, such as a core or slice of given dimensions, as a *sampling unit* (37). Sampling units also vary among themselves both vertically and horizontally and for purposes of sampling may be treated as individuals (33).

A sample consists of all sampling units drawn to represent a single soil population. If all sampling units of a soil could be evaluated, each characteristic of a soil population could be defined in terms of a set of stable numbers, *parameters*, such as a mean, a range, and a standard deviation. Parameters of a soil population cannot feasibly be measured, but they can be estimated by a similar set of numbers, *statistics*, for the population of a sample that represents the whole (29). Unfortunately, too many investigators treat statistics as

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parameters and fail to test, or even consider, the probable degree of accuracy of the estimate.

The accuracy with which a soil sample represents the population sampled depends upon the soil variability, the number of sampling units contributing, and the way in which the sample is drawn (22). If at least two sampling units are drawn and evaluated separately, the variability of the population and the reproducibility of the sample mean can be estimated. The statistical relationships upon which those estimates depend provide a basis for sound sampling procedure.

The standard deviation (s) of a sample population is a measure of population variability and is calculated by the formula

$$s = \sqrt{Sx^2/(n-1)} \quad (1)$$

in which x is deviation of each sampling unit from the sample mean (\bar{x}), S indicates summation, and n is the number of sampling units. The standard error (s_x) or "standard deviation of the mean" is a measure of reproducibility of the sample. It is related to standard deviation by the formula

$$s_x = s/\sqrt{n}, \text{ which may be written } s_x = \sqrt{Sx^2/n(n-1)} \quad (2)$$

The interval $\bar{x} \pm s$ includes approximately two thirds of the *sampling units* of a normally distributed sample population; the interval $\bar{x} \pm s_x$ includes approximately two thirds of the *means* of similarly drawn samples. The ratio of the difference between the means of two similarly drawn samples (D) to standard error of this difference (s_d) defines "t values,"

$$t = D/s_d \quad (3)$$

from whose frequency distribution for a given size of sample the probability of occurrence in sampling can be estimated. The standard error of the difference between two means is calculated by the formula $s_d = \sqrt{s_{\bar{x}a}^2 + s_{\bar{x}b}^2}$, in which $s_{\bar{x}a}$ and $s_{\bar{x}b}$ are the respective standard errors of the two means. When estimating the reproducibility of a sample mean, an investigator wishes to know the error of the difference between means of samples composed of the same number of sampling units and can often assume that the standard errors of the two samples are approximately equal. Under these conditions $s_d = s\sqrt{2}$, which can be reduced to $s_d = s\sqrt{2/n}$ by substituting from equation (2). Then equation (3) can be written $t = D/s\sqrt{2/n}$, or

$$n = 2t^2s^2/D^2 \quad (4)$$

These are relationships upon which accurate definition of the sample population and estimates of fiducial limits and significance depend. They should, therefore, be bases for determining sound sampling methods. A further useful approximation for a sample is the relationship of standard deviation to the range of a normally distributed population,

$$s = (r_n - r_1)/C \quad (5)$$

in which C is a constant—approximately 3, 4, 5, and 6 for 10, 25, 100, and 500 sampling units respectively—and r_n and r_1 are the extremes of the range (23, 29).

SAMPLING VOLUME

A sample that consists of sampling units from two distinctly different populations is representative of neither. Subdivision of heterogeneous populations into *homogeneous strata* is one of the most effective methods of increasing the

accuracy of sampling (7). Several small samples, each from a homogeneous part of the whole, yield more precise information than a single large sample (29). When applied to soils, the conventional concept of homogeneity (23, 29) must be conditioned by the fixed, three-dimensional variation of soils. It must be applied to *sampling volumes*. For obvious practical reasons, only oriented subdivision, vertically and horizontally, is feasible or significant. Sampling units that contribute to a given sample should be confined vertically to a horizon, or part of a horizon, that does not vary significantly for the objective with depth; they should also be confined horizontally to an area that can be treated as a unit for the objective. A horizon of a soil type within a given area is an example of a sampling volume that is "homogeneous" with respect to certain easily observed characteristics. If one samples beyond its limits, either vertically or horizontally, the precision of the estimate of those characteristics may decrease with an increase of sample size.

Horizontal subdivision

Within restrictions of cost and minimum size of area significant for the objective, soil volumes to be studied should be subdivided horizontally to provide *sampling areas* that are homogeneous with respect to soil type (19, 20, 32), plant growth (31, 32), and treatment (13, 32). If the area is large and apparently uniform with respect to all of these factors, it may still be heterogeneous with respect to the chemical characteristic under test. Large, apparently uniform areas should be subdivided arbitrarily within the limits of cost and significance of size for the objective (14, 32). For field experiments the minimum subdivision feasible may be an experiment, a block, or a plot; for a "soil-testing service" it may be the minimum area a farmer will treat as a unit. Generally it will be some compromise between the minimum desired for accuracy and that required for economy. Hossack (14), for example, found $\frac{1}{2}$ acre a desirable unit but 2 acres the minimum economically feasible for fertility diagnosis in cane fields.

Vertical subdivision

Recognizable horizons of the same soil type represent different populations both physically and chemically and are logical units of vertical subdivision (19, 20, 30). Data of tables 1 and 2 show differences of both amount and variability of constituents by horizons and indicate how incorrect any inferences drawn from composites of two horizons might be. Many conflicting results that appear in the literature are due to mixing unlike horizons (8,19). Physical homogeneity vertically does not insure chemical homogeneity, however, and certain objectives require vertical subdivision of apparently uniform horizons. Askew (3) found subdivision of the surface horizon necessary for accurate characterization of fertilized pasture soils. Piper (25) recommends sampling only a thin layer in the middle of each horizon, and Winters² reports that arbitrary subdivision of recognized horizons into 3-inch layers is needed for soil-genesis studies.

² From private correspondence with Eric Winters, head, department of agronomy, University of Tennessee.

TABLE 1

*Potassium determined by rapid chemical methods on single cores from a 12- by 36-foot plot on Volusia gravelly loam, October 1943**

K in pounds per 2,000,000 pounds soil

ROW	A						B						MEAN
Site	1	2	3	4	5	Mean	1	2	3	4	5	Mean	
0 to 6 inches:													
Core 1.....	50	100	100	100	100	90	85	125	160	130	85	115+	100+
Core 2.....	80	80	125	70	55	80+	75	95	115	80	90	90+	85+
Mean.....	65	90	110+	85	75+	85+	80	110	135+	105	85+	100+	95
B ₂ horizon:													
Core 1.....	50	60	65	65	55	55+	50	50	60	55	40	50+	55
Core 2.....	55	40	65	65	40	50+	60	65	70	55	55	60+	55+
Mean.....	50+	50	65	65	45+	55+	55	55+	65	55	45+	55+	55+

* Samples were single auger cores. Rows A and B were straight north-south lines 6 feet apart in the middle of interspaces between corn rows, parallel to the long axis of the plot and parallel to the direction of cultural operations. Sites were 6 feet apart in rows A and B. Cores 1 and 2 were taken 6 inches apart at each site. Samples of the highly mottled friable B₂ horizon were drawn after reversing the auger one-half turn when the underlying compact semi-cemented "hardpan" was encountered. Special precautions were taken to prevent contamination. Two years prior to sampling, 150 pounds of KCl an acre was applied for winter wheat harvested in 1942. In May, 1943, 2000 pounds of ground limestone and 6 tons of manure an acre were plowed down for corn. Analysis was by rapid chemical methods of Peech and English (24).

TABLE 2

*Calcium determined by rapid chemical methods on single cores from a 12- by 36-foot plot on Volusia gravelly loam, October 1943**

Ca in pounds per 2,000,000 pounds soil

ROW	A						B						MEAN
Site	1	2	3	4	5	Mean	1	2	3	4	5	Mean	
0-6 inches:													
Core 1.....	1600	2000	2700	2200	1700	2040	4250	4500	5000	4500	4500	4500	3295
Core 2.....	2600	2250	2000	1900	1000	1950	2200	3500	2600	1700	1200	2240	2095
Mean.....	2100	2125	2350	2050	1350	1995	3225	4000	3800	3100	2850	3395	2695
B ₂ horizon:													
Core 1.....	600	600	800	700	600	660	900	600	600	700	800	720	690
Core 2.....	600	450	600	500	600	550	900	650	900	600	600	730	640
Mean.....	600	525	700	600	600	605	900	625	750	650	700	725	665

* See table 1 for description of area and methods.

NUMBER OF SAMPLING UNITS

Within a homogeneous soil population, the accuracy of the estimate is a function of the number of sampling units drawn and the variability of the population [see equation (2)]. Too often the number to be drawn is decided arbitrarily. Studies of numbers required for reliable estimates (6, 9, 11, 16, 33, 34) indicate large differences among soils and show a need for larger numbers than are commonly specified in directions for sampling (2, 12, 15, 21, 32).

An estimate of required numbers on the basis of valid statistical principles is preferable to arbitrary judgment, even though available data are not precise. If variability is known or can be estimated, an estimate of numbers required for a specified degree of accuracy can be made by means of equations (4) and (5). In table 1, the range of potassium in the 0- to 6-inch layer is 110 pounds for 20 sampling units. If the range is assumed to be no greater than 120 pounds for 25 sampling units, equation (5) becomes $s = 120/4 = 30$. This value is a reasonably good estimate of population variability. Then if the maximum sampling error permissible [D in equation (4)] is chosen as 20 pounds of potassium, and a t value of 2.1 for the 5 per cent level and 18 degrees of freedom, the smallest number likely to be required, is selected from a "table of t ," equation (4) becomes $n = (2)(4.4)(900)/400 = 20$ sampling units required. For calcium in the 0-6-inch layer (table 2), the range is 4,000 pounds. By equation (5), s would be about 1100. Assuming the maximum error permissible to be 200 pounds and selecting a t value of 2 for the 5 per cent level and 30 or more degrees of freedom, equation (4) becomes $n = (2)(4)(1,210,000)/40,000 = 242$ sampling units, an excellent example of heterogeneity due to treatment. Even a rough estimate of the range provides an acceptable estimate of the size of sample required.

SELECTING THE SAMPLE

Three general principles should be kept in mind when selecting sampling units: (a) A sample composed of few sampling units scattered at random throughout a homogeneous population contains information up to the limits of its size, but even a large sample, confined to a part of the population, contains no information about the excluded parts. (b) An unbiased estimate of the mean requires that every *sampling unit* have an equal chance of being drawn. (c) An unbiased estimate of significance and fiducial limits requires that every *sample of n sampling units* have an equal chance of being drawn (29).

For objectives involving an estimate of fiducial limits, complete randomization is necessary to meet restriction (c). Numbers required for tests of this kind are generally great enough that restriction (a) would automatically be met by a random sample. If circumstances limit numbers, bias of a small sample should not be ignored for the sake of complete randomization (17). It is well to emphasize that walking "at random" over an area when selecting sampling units is far from complete randomization and is subject to strong personal bias.

For objectives that require only an unbiased estimate of the mean, incomplete

randomization by means of a grid superimposed at random satisfies principle (b). Use of a grid gives every sampling unit, but not every possible combination of n sampling units, an equal chance of being drawn. *This method requires special precautions to avoid bias from superimposing the grid parallel to some systematic variation in the soil.* In table 2, for example, the mean for calcium in the plowed layer appears to be biased by one core of each pair in row B cutting a zone of concentration of ground limestone as a result of superimposing the grid parallel to the direction of cultural operations. Aside from restrictions of use of data and precautions to avoid bias, sampling according to a grid has many advantages. It insures sampling units for a small sample from all parts of the area. If sampling units, or several composites of them from geographically associated areas, are analyzed separately, it permits cartographic expression of different levels of the characteristic determined. Probably it is safer to instruct nontechnically trained men to sample by a grid than to sample "at random" (17, 29).

It is possible that selection of sampling units with no pretext of randomization may give a good estimate of a mean at a minimum of cost. The most experienced individuals are generally unable to select without bias, however, even with an intimate knowledge of the population (7). Data from selected samples cannot be used for estimates of fiducial limits (29). Selection has its place in soil sampling where only small samples are feasible and where chemical characteristics of modal profiles of a soil type are to be determined. In the latter case, a modal profile may be selected with a number of independent profiles to establish variation (25).

SAMPLING WITH TIME

Chemical properties of soils vary not only vertically, horizontally, and with treatment but also with time. Horton and Stinson (13) found 25 sampling units adequate 1 year after fertilization where 100 were required during the first 3 weeks. Bear and McClure (6) stressed the importance of sampling the same sites in studies of behavior of plant nutrients with time. Filingier (8) attributed conflicting results reported for behavior of nitrogen in orchard soils to lack of uniformity of time of sampling. Unpublished data of Peech show wide seasonal fluctuation of exchangeable potassium as determined by rapid chemical methods (24). If any of those characteristics that are subject to seasonal variation are studied over a period of years, it is imperative that samples compared be taken at the same season and that possible effects of varying weather conditions or crops be considered.

COMPOSITE SAMPLES

Compositing consists of mixing sampling units for a single analysis of the mixture on the assumption that a result from the composite is a valid estimate of a mean of results from the sampling units contributing. It is a common expedient to obtain numbers large enough to represent the sampling volume accurately without the expense involved in analyzing each sampling unit separately. Compositing is valid only if (a) the sampling volume represents a homo-

geneous population, (b) equal amounts of each sampling unit contribute to the subsample analyzed, (c) no interactions that would affect the results materially occur, and (d) an unbiased estimate of the mean is the only objective.

It is obvious that the value obtained by a single analysis of a subsample from a composite is weighted by the amount of soil contributed by each sampling unit. Problems of mixing and subsampling are discussed under preparation of the sample. The variability of subsamples can be checked by analyzing more than one.

Values obtained from composites have been shown to agree well with means of values obtained from single sampling units in analysis for total carbon, nitrogen, and phosphorus (27, 34). If sample treatment prevents loss by volatilization, the error of compositing for determination of the total of a constituent would be due to inefficient compositing and subsampling. For such determinations as pH, "available" nutrients, and exchangeable cations, however, interactions are possible sources of error. Easily soluble phosphorus, for example, of one soil might be fixed in a composite by the addition of sampling units from another soil having a high phosphorus-fixing capacity. It appears, however, that such errors would be insignificant for a homogeneous population compared to those of sampling and subsampling.

If one is interested only in an unbiased estimate of the mean, compositing appears to be a logical procedure. The opportunity it offers for increasing the accuracy of the estimate by the use of larger numbers of sampling units per sample than could be analyzed individually far outweighs probable inaccuracies. Compositing also makes it possible to obtain reliable mean values for a large number of soils at relatively small expense.

If any statistic other than the mean is required, a single composite sample is completely inadequate. For some objectives knowledge of variability is equally as important as knowledge of the mean (33, 34, 38). Note in tables 1 and 2 how averaging results from even two sampling units obscures variability. The range of means decreases in proportion to the square root of the number of sampling units contributing (29). If separate composites are made for different parts of an area, variability among the parts can be estimated, but variability within each part or for the population as a whole is completely obscured.

If two or more composite samples are drawn in the same way to represent the same sampling volume, their reproducibility can be estimated by equation (1), in which x is the deviation of composite values from their mean, n is the number of composite samples, and s is the standard deviation of composite values. If a composite value can be considered an approximation of the mean of values of the sampling units contributing, a standard deviation of composites can be considered an approximation of the standard deviation of means, or standard error, with respect to the population of sampling units. Standard deviation of sampling units can then be approximated by solving for s in equation (2), $s = s_{\bar{x}} \sqrt{n}$, by substituting the standard deviation of composite values from equation (1) for $s_{\bar{x}}$ and the number of sampling units contributing to each composite for n . This method is subject to considerable error unless the number

of composite samples is large, but it can be used to obtain a useful approximation of variability among sampling units.

Compositing either vertically or horizontally for studies of morphology and genesis of soils can seldom be justified (25). Such studies involve relationships among horizons at a particular place. Likewise, the possibility that compositing may obscure soil-plant relationships in studies that involve two or more horizons should be considered carefully.

SAMPLING TOOLS

A sampling tool should provide a sampling unit that is (a) uncontaminated, (b) approximately uniform in cross section to the desired depth, and (c) reproducible. Tapered cores or slices may bias the estimate of a mean for the unit by unequal weighting if systematic variations with depth are significant. Dissimilar cores in successive samplings also bias the estimate of the mean for a composite by unequal weighting of different parts of an area.

The indexes of the *Experiment Station Record* and *Chemical Abstracts* furnish an extensive bibliography of special sampling tools. Three principal types are used: (a) blades—trowels, spades, shovels, spoons, and knives; (b) tubes—open-sided and plain-cylinder; constricted-tip and uniform-bore; and (c) augers—wood-bit, post-hole, and sheathed (32).

In sampling with blades, a slice of uniform cross section should be taken from the face of a clean fresh vertical cut between the limits of depth chosen. Road cuts and similar excavations are generally contaminated and should not be used. With good technique, the method gives uncontaminated, unbiased sampling units and permits supplementary observations of the undisturbed soil to be made. It can be used under almost all soil conditions except below a water table and is especially well suited to studies of soil morphology and genesis (25). The procedure is labor- and time-consuming, however, and the restrictions it imposes on numbers more than offset its advantages for many objectives (9).

Sampling tubes are cylinders in which a core enters the barrel as the tube is forced into the soil by direct vertical pressure. The core is generally somewhat compacted (10). Tubes with constricted tips cut a core slightly smaller than the bore, thereby facilitating removal. Open-sided tubes permit observation of the core before removal. Sampling tubes take a core of uniform cross section, minimize contamination, and permit rapid sampling in soils to which they are adapted. They are difficult to use in stony, dry, very heavy, or very sandy soils.

Ordinary wood augers can be used in moist soils that are too stony or heavy for sampling tubes. They will not hold a satisfactory core in dry soils; their cores are not uniform and are easily contaminated. Each core should be stripped to the size of the bit to provide as nearly uniform cross section as possible and remove contaminating material. In sampling subsoils, the upper 2 or more inches is mixed with material from overlying horizons and should be discarded. Other sampling tools are generally to be preferred. Ordinary post-hole augers, with combined cutting and digging edge and partly sheathed body, are preferred

by many workers (25). They can be used in dry or very sandy soils that cannot be sampled with a tube or wood auger. Their taper causes unequal volumes to be taken from different depths, however, and results in contamination of subsoil samples with material from overlying horizons. A completely sheathed, parallel-sided auger that operates on the same principle minimizes contamination and takes a sampling unit of uniform cross section. It has many of the advantages of sampling tubes and can be used throughout a wider range of soil conditions, but like other augers, it almost completely destroys soil structure for supplementary observations.

PREPARATION OF THE SAMPLE

When a gross sample has been drawn, chemical reactions and contamination that would affect results of analysis must be held to a minimum. A subsample that accurately represents the whole must be drawn, generally after reduction of the gross sample to a size and form convenient for stock.

Preservation

Most authorities recommend air-drying to reduce the rate of possible reactions in the disturbed soil (4, 25, 28, 36). The sample should not remain moist for extended periods, and clods should be crushed to facilitate drying. Drying at high temperatures may affect the analysis. Chemical reactions in air-dry soil stored for prolonged periods are generally assumed to be negligible, but they are possible sources of error for some determinations and deserve special study.

Contamination of samples by absorption of gases is an important source of error that is often overlooked. Stock samples exposed to the air in a laboratory, for example, may absorb significant amounts of ammonia in a short time. Samples should be dried in an atmosphere containing no gases that are possible sources of contamination and should be placed in closed containers as soon as they are dry. Containers should be clean and composed of materials that will not contaminate the sample. Air-dry stock samples should be kept in closed containers and exposed to the air as little as possible.

Marked increases of ammonia when the soil is air-dried are reported by Richardson (26); Piper (25) recommends immediate analysis of the moist sample for ammonia and nitrates. Piper also reports rapid drying at 55°C. to be preferable to air-drying for determinations of ammonia and nitrates and suggests the use of toluene to stop microbiological activity if the moist soil cannot be analyzed or dried at once.

Reduction of sample size

The sample should be regarded as a population the composition of which varies widely among particles—from that of primary minerals such as quartz to that of clay minerals or organic matter. The size distribution of primary particles varies widely among minerals of different chemical composition; for example, quartz is concentrated in the large and clay minerals in the small particle-size fractions. Aggregation of small particles reduces the systematic

variation of chemical composition with particle size in a sample but contributes greatly to heterogeneity within a given fraction. The whole heterogeneous mixture must be reduced in size and subsampled in such a way that a single analysis gives an unbiased estimate of the mean of the entire gross sample. This objective requires that every particle have an equal chance of being drawn (29). If the requirement of chance is met, the accuracy with which a subsample can be drawn depends upon its size and the heterogeneity of the population [see equation (2)].

TABLE 3

*Relationship of sampling error to size-weight percentage of coal analyzed for ash**

Adapted from Bailey (5)

Weight of subsample.....gm.	1	1	144	35.2	2.26
Mesh of sieve used before dividing.....	200	80	8	8	8
Size-weight percentage†.....	0.0002	0.0014	0.008	0.034	0.53
Sampling error, odds 1:1 (per cent of subsample).....	0.02	0.07	0.18	0.33	0.60
Sampling error, odds 19:1‡ (per cent of subsample).....	0.06	0.21	0.54	0.99	1.80

* 11.50 per cent ash including about 5 per cent slate fragments.

† $100 \text{ (average weight of largest pieces)}/(\text{weight of subsample})$.

‡ Calculated at three times probable error.

TABLE 4

Limits of subdivision of coal samples of different degrees of fineness for a sampling error less than 0.54 per cent in 11.50 per cent ash at odds of 19:1

Adapted from Bailey (5)

SIEVE	SIEVE OPENING	MINIMUM SUBDIVISION
<i>meshes/inch</i>	<i>mm.</i>	<i>gm.</i>
2	10.80	8300
4	6.35	1100
8	2.54	120
10	1.93	55
20	0.91	3

Bailey (5) has shown that the subsampling error for material of a given degree of heterogeneity is a parabolic function of the ratio between average weight of the largest particles and weight of the subsample. The magnitude of that error for a sample of coal is indicated in table 3. The relationship of particle size to limits of subdivision for a given sampling error is shown in table 4. Although these data cannot be applied directly to soils, they demonstrate the need for standards of soil sampling similar to those published for coal (1).

An efficient method of subdividing a large gross sample to a size suitable for stock is well illustrated in A.S.T.M. standards (1). Successive crushing, screening, mixing, and subdividing of the half retained at each subdivision obviates

the need for crushing the entire sample to the final particle size. Crushing instruments, such as a hardwood rolling pin or a rubber-capped pestle and iron, porcelain, or agate mortar may be used to crush aggregates without appreciable breaking of primary particles (25, 28, 35). Piper (25) lists an end-runner grinding mill fitted with hardwood pestle and rubber lining among efficient instruments. Large primary particles and organic residues retained by the sieve may be weighed separately or discarded according to requirements of the objective. The sieved material should be thoroughly mixed by rolling or successive coning (1) and subdivided by quartering (1) or with a riffle sampler (35). Bailey (5) found use of a riffle sampler to be more efficient than quartering. All mortars, grinders, sieves, and containers should be clean and constructed of materials that will not contaminate the sample (25).

The stock sample

Tentative standards of the Association of Official Agricultural Chemists (4) call for analysis of material passing a $\frac{1}{2}$ -mm. sieve. Investigators of the U.S. Department of Agriculture and many others in this and other countries analyze material passing a 2-mm. sieve (25, 28, 36). Several soil chemists use the fraction less than 1 mm.

Results obtained by analysis of material passing different sieves are not necessarily comparable. Resistant soil minerals are segregated in the larger particle-size fractions. Coarse primary particles retained by fine sieves are discarded, biasing the stock sample in favor of fine particles and reducing the base upon which results are calculated. Data of mechanical analysis show that the fraction between 1 and 2 mm. in diameter is negligibly small for most soils but may be significant for soils like Iredell loam and Sassafras sandy loam, in samples of which it amounted to 10.7 and 18.2 per cent respectively. The fraction between $\frac{1}{2}$ and 2 mm. amounted to 10 per cent of a sample of Hagerstown silt loam, 18 per cent of Gloucester fine sandy loam, and 65 per cent of Sassafras sandy loam (20). Obviously, a standard of maximum particle size for chemical analysis is needed.

The maximum particle size should permit drawing the size of subsample required by the analytical procedure with the degree of accuracy required by the objective. There is little doubt that 1- or 2-gm. samples required by modern micromethods cannot be drawn by common procedures from material passing a 2-mm. sieve without significant error for some determinations. Material passing a 1-mm. sieve probably can be subsampled accurately, but $\frac{1}{2}$ -mm. maximum size gives a needed margin of safety. Research is needed to establish definitely the maximum particle size of material from which a given size of subsample can be drawn accurately.

Material passing a 2-mm. sieve has a distinct advantage over smaller sizes in representing more accurately the total volume of soil. It includes a fraction very important physically, if not chemically, that is discarded from finer sieves. It corresponds to an internationally accepted standard for mechanical analyses, and its abandonment would mean that some part of the accumulated analytical

results throughout the world would not be directly comparable to results of future analyses. The discrepancy would be significant in few cases for 1-mm. material but would involve a high proportion of soils for $\frac{1}{2}$ -mm. material.

The conflict between accurate representation of the sampling volume and accuracy with which a small subsample can be drawn can be overcome in most cases. For those determinations not affected by grinding of primary particles, 2-mm. material can be ground to any size needed for accurate subsampling. For many determinations affected by grinding, it can be assumed that the fraction less than 2 mm. and greater than the maximum size permitted for accurate subsampling does not contribute a significant amount of the constituent to be determined (as is assumed when the fraction is discarded). That fraction can be weighed, and results of analysis can be expressed on a standard base of all material less than 2 mm. In some cases, a large subsample can be drawn and leached or extracted, and an aliquot of the solution can be taken for analysis by micromethods.

SUMMARY

The error due to sampling of soils is generally greater than that due to analysis. Statistics provide a basis for sound sampling procedure. The soil may be considered a population of sampling units that vary among themselves both vertically and horizontally. The first step in a sound sampling method is to subdivide the population into homogeneous strata. Within a homogeneous stratum the number of sampling units needed is a function of variance and required degree of accuracy and can be estimated from knowledge of the range or of variance by means of the relationship of *t* values to standard error and the maximum sampling error permissible. Complete randomization is necessary for estimates of significance or fiducial limits, but incomplete randomization gives an unbiased estimate of the mean. A selected sample may be most efficient for certain objectives. Time is an important factor in sampling for some objectives. Compositing of sampling units is an efficient expedient to obtain adequate numbers at low cost, but single composite samples can be used only if an unbiased estimate of the mean is the only objective. Sampling tools are discussed with respect to their ability to provide unbiased and uncontaminated samples. Methods of reduction of the gross sample to a stock sample and subsampling for analysis should be based on the relationship of sampling error to particle size and size of subsample. A standard maximum particle size for chemical analysis is needed.

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THE RAPID DETERMINATION OF TOTAL NITROGEN IN SOIL¹

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In the use of a method previously reported,² for determining total nitrogen in soil by oxidation to nitrate, it was found that amide nitrogen and ammonia nitrogen were not oxidized and total nitrogen was not determined in soil that contained these forms. In the modified process proposed in this paper amide nitrogen is hydrolyzed to ammonia and the ammonia nitrogen is combined as glycine by means of monochloroacetic acid, the amino acid group being readily oxidizable to nitric acid so as to be included in the phenoldisulfonic estimation of nitrate nitrogen.

PROCEDURE

Place 100 mgm. of finely ground soil in the bottom of a test tube (20 by 150 mm.) and add 1 cc. of 40 per cent sodium chlorate solution without wetting the sides of the tube. Slant the tube and allow 1 cc. of fuming sulfuric acid (15 per cent SO_3) to run down the side slowly with shaking. The reaction is vigorous, but if the tube is held slanting and the acid is added carefully, no solution is lost. When reaction has ceased, add a measured quantity of water (8 cc. for soil of medium nitrogen content, 3 cc. if the soil is low in nitrogen, or 18 cc. if it is exceptionally high), shake well, and allow to settle.

Place 1 gm. of monochloroacetic acid in a dry tube, add 0.5 cc. of the supernatant liquid from which the heavy silica residue has settled, and shake well. Add 1.5 cc. of 40 per cent NaOH solution and shake well. As soon as the monochloroacetic acid is dissolved, add 0.3 cc. of 40 per cent sodium chlorate solution and shake. Then add 2.5 cc. of fuming sulfuric acid slowly, at a rate to cause moderate boiling. A yellow color should form and persist. Shake and blow out fumes with a bent glass tube until most of the chlorine is gone and only a faint yellow color, or none at all, is left. Cool somewhat and add 2.5 cc. of phenoldisulfonic acid. Mix well and wash into a 50-cc. volumetric flask with 15 to 20 cc. of water. Add carefully a small excess of 40 per cent NaOH solution as indicated by the maximum yellow color. Cool, make to 50 cc., mix, and pass through a dry filter paper. Compare in a colorimeter with a standard and a blank carried through the same procedure as the unknown. From these readings calculate the nitrogen in the sample. For soil high in nitrogen, a standard containing 0.0025 mgm. N per cubic centimeter should be used; for low-nitrogen soils, the standard should be half this amount.

¹ The investigation reported in this paper is in connection with a project of the Kentucky Agricultural Experiment Station and is published by permission of the director.

² Emmert, E. M. A rapid method for determination of total nitrogen in soil. *Soil Sci.* 38: 139-142, 1934.

REMARKS

With some soils, especially those high in organic matter, the reaction may be vigorous. Although the oxidation with heat generated by fuming sulfuric acid can be performed on these soils, some may prefer to use boiling water, which gives a less violent reaction and requires less individual attention. To 100 mgm. (more, if the soil is low in nitrogen and organic matter) of finely ground soil in a test tube, add 1 cc. of 40 per cent sodium chlorate solution and 3 cc. of 60 per cent by volume sulfuric acid. Place in boiling water for about 5 minutes, shaking occasionally. Dilute the solution to an appropriate volume with water as directed in the procedure in which fuming sulfuric acid was used. Treat 0.5 cc. of the supernatant liquid with monochloroacetic acid as directed above. A distinctly yellowish coloration when phenoldisulfonic is added (light brown, dis-

TABLE 1

Total nitrogen determination in soils by the proposed method in comparison with the Kjeldahl
Parts in 2 million pounds of air-dry soil

SOIL	KJELDAHL	PHENOLDISULFONIC
1	2,044	2,082
2	3,438	3,472
3	2,322	2,326
4	1,155	1,176
5	3,564	3,556

TABLE 2

Nitrogen recovered from pure ammonium chloride by the proposed method

	ADDED	FOUND
	mgm.	mgm.
Solution alone.....	0.500	0.50400
Solution alone.....	0.250	0.25200
Solution alone.....	0.125	0.12600
Solution added to soil.....	0.001	0.001030
Solution added to soil.....	0.001	0.000996

appearing on dilution, does no harm) should not occur, since off-color tints will form. (Chlorate on the sides of the tube and weak fuming acid will cause this.)

The results agreed closely with those obtained by the Kjeldahl method, as shown in table 1. The figures are averages of several determinations. For instance, soil 5 gave 3582 and 3530, the average being 3556, or almost that of the Kjeldahl value.

In order to show that ammonia is recovered, tests for it were made in pure ammonia solutions and for ammonia added to soils. Table 2 indicates good recovery, showing that monochloroacetic acid takes up the ammonia freed by NaOH and forms glycine, the amino group being easily oxidized to nitric acid.

The method is satisfactory on the soils studied, but it has not yet been tried in a very wide range of soils.

NOTE ON THE ROOT-NODULE BACTERIA OF *ASTRAGALUS SINICUS* L.

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On the basis of a fairly extensive cross-inoculation study of the wild leguminous plants in Wisconsin, Bushnell and Sarles (2), reported that none of the four species of *Astragalus* studied [*A. alpinus* L., *A. canadensis* L., *A. caryocarpus* Ker., and *A. neglectus* (T. & G.) Shelden] was assigned to any tested cross-inoculation group, and pointed out that "these results, although they do not warrant the establishment of a new cross-inoculation group for *Astragalus* spp., do lend weight to the probability that *Astragalus* spp. make up their own select cross-inoculation group." This is the only published record relating the cross-inoculation characteristics of the genus *Astragalus*, notwithstanding the fact that *A. sinicus* is one of the major green manuring and forage crops in China and Japan. It is not mentioned in Itano's book on soil microbiology (3) or in Junk-Opppenheimer-Weisbach's *Tabulae Biologicae* (5).

The present note is a summary of inoculation tests carried out during the last 3 years on the strains of root-nodule bacteria isolated from *A. sinicus* and other plants and their nodule-forming properties.

Morphologically and culturally, our strains of *A. sinicus* bacteria conform well with those described by Aso and Ohkawara (1) and by Itano and Matsuura (4) and with Bushnell and Sarles' bacteria of other *Astragalus* species (2). They are all gram-negative, uniformly stained when young, are in the form of coccoid rods smaller than pea bacteria, and are motile. On yeast-mannitol agar slants, they grow more slowly than pea bacteria and more rapidly than most cowpea and soybean bacteria. A moderately abundant growth is often obtained after 1 week's incubation at 25°-30° C. On yeast-mannitol congo-red agar plates, the colonies are round, raised, whitish, moist, gummy, and unstained by congo-red. On calcium-glycerol-phosphate agar, they grow moderately abundantly and are moist and opaque. On Clark and Lub's medium, they are turbid with gummy deposit. They turn litmus milk alkaline and give a clear serum zone. On potato strip medium, they grow moderately abundantly and are milky white, watery, and glistening.

In the inoculation tests, plants of *A. sinicus* were grown in sterilized sand containing modified Crone's solution and were inoculated with various strains of root-nodule bacteria. The sterileness of the culture medium was checked in each case with uninoculated controls. A total of 30 strains of bacteria of known cross-inoculation groups representing the seven major groups, and also six strains of bacteria isolated from root nodules of *A. sinicus*, were used in the tests. The results are summarized in table 1. Repeated experiments showed consistently that *A. sinicus* formed nodules only with bacteria isolated from the same plant

species and with a strain of cowpea bacteria isolated from nodules of *Desmodium heterophyllum*.

TABLE 1

Summary of root-nodule formation of different strains of bacteria on A. sinicus

STRAIN	SOURCE OF ISOLATION*	CROSS-INOCULATION GROUP	NODULE FORMATION
107	<i>Vicia hirsuta</i>	Pea	—
108	<i>V. sativa</i>	Pea	—
110	<i>Vicia</i> sp.	Pea	—
114	Sweden commercial	Pea	—
201	<i>Trifolium pratense</i>	Clover	—
205	<i>Trifolium</i> sp.	Clover	—
301	<i>Melilotus indica</i>	Alfalfa	—
306	<i>M. indica</i>	Alfalfa	—
302	<i>Medicago hispida</i>	Alfalfa	—
303	<i>M. sativa</i>	Alfalfa	—
304	<i>M. sativa</i> , Wisconsin 107	Alfalfa	—
305	<i>M. sativa</i> , New Jersey A2	Alfalfa	—
401	<i>Soja max</i>	Soybean	—
S1	<i>S. max</i>	Soybean	—
S2	<i>S. max</i>	Soybean	—
501	<i>Cajanus cajan</i>	Cowpea	—
507	<i>Lespedeza striata</i>	Cowpea	—
508	<i>Pueraria hirsuta</i>	Cowpea	—
510	<i>Indigofera suffruticosa</i>	Cowpea	—
511 B	<i>Phaseolus aureus</i>	Cowpea	—
516	<i>P. aconitifolius</i>	Cowpea	—
512	<i>Vigna sinensis</i>	Cowpea	—
515	<i>Crotalaria striata</i>	Cowpea	—
517	<i>Alysicarpus vaginalis</i>	Cowpea	—
520	<i>A. vaginalis</i>	Cowpea	—
519	<i>Atylosia scarabeoides</i>	Cowpea	—
521	?	Cowpea	—
522	<i>Desmodium heterophyllum</i>	Cowpea	+
523	<i>Derris elliptica</i>	Cowpea	—
701	<i>Phaseolus vulgaris</i>	Bean	—
601	<i>Astragalus sinicus</i>		+
602	<i>A. sinicus</i>		+
603	<i>A. sinicus</i>		+
604	<i>A. sinicus</i>		+
605	<i>A. sinicus</i>		+
606	<i>A. sinicus</i>		+

* The writers acknowledge the assistance of C. J. Wang, who kindly identified the host plants.

SUMMARY AND CONCLUSIONS

The present investigation forms the counterpart of Bushnell and Sarles' work, in which bacteria isolated from *Astragalus* spp. were tested on plants of known cross-inoculation groups. The results agree, in that root-nodule bacteria of

Astragalus do not produce nodules on other genera of leguminous plants, nor do bacteria isolated from other sources, except *Desmodium heterophyllum*, form nodules on *Astragalus* plants. Since it is well known that bacteria of the cowpea group often infect plants of different groups, the nodulation of *A. sinicus* by *D. heterophyllum* bacteria should not be regarded as invalidating the conclusion that *Astragalus* and its root-nodule bacteria must be considered as a select cross-inoculation group.

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THE IMPORTANCE OF OXYGEN IN THE NUTRIENT SUBSTRATE FOR PLANTS—ORGANIC ACID¹

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The importance of the organic acids as possible intermediates, precursors, or end products in the metabolism of plants has long been a topic of much theoretical discussion but based perhaps on inadequate quantitative experimental evidence. In recent years, however, with the new developments in the estimation of these acids as a group, and methods of quantitatively determining some of the important individual constituent acids, a clearer insight has been gained into the functions, mechanisms, and causes of production of these acids. The literature on this subject has recently been the basis of some very excellent reviews (1, 2, 18), and a discussion of the role of the organic acids in protein metabolism has been provided by Chibnall (4) and by Vickery *et al.* (17, 19).

Since the present paper is part of a general investigation on the effect of dissolved oxygen in the nutrient substrate on the nutrition and metabolism of plants, emphasis is placed on the question of the relation between oxygen and organic acids in the presentation of the results of the investigation, rather than on the transformations and the immediate role of organic acids in the economy of the plant.

EXPERIMENTAL METHODS

Oat (var. Keystone) plants were grown by the methods employed in this laboratory for the production of experimental plants. Full details of the cultural methods are given by Gilbert and Shive (9). Briefly, the procedure was as follows:

Four levels of dissolved oxygen were maintained in the nutrient solutions by bubbling through them, at a sufficiently rapid rate, appropriate mixtures of oxygen and nitrogen to give oxygen levels in the substrate of 0, 4, 8, and 16 p.p.m. These concentrations were maintained well within 25 per cent variations of the indicated concentration.

All the experimental plants were grown for 20 days in a culture solution at an oxygen level maintained at the saturation point in equilibrium with the atmosphere (approximately 8 p.p.m.). At the end of this period the plants were placed on experimental treatment for 10 days.

Formula I of Shive and Robbins (13) was used as a basis for the nutrient medium, but $(\text{NH}_4)_2\text{SO}_4$ was omitted and nitrogen was supplied only as the nitrate.

At the beginning of the experimental period the six plants of one culture in

¹ Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of plant physiology.

duplicate were harvested and dried at 70°C. for 48 hours. The plants of this culture are designated as "original." The plants in half of the remaining cultures were continued in the same culture solution and placed on treatment at the various oxygen levels above indicated. These are designated the "plus-nitrate" plants, or series I. The plants of the remaining cultures were placed in a solution without nitrate and grown at the several oxygen levels. These are designated the "minus-nitrate" plants, or series II. At the end of the experimental period of 6 days, one culture of series II at each oxygen level, except 16 p.p.m., was supplied with nitrate-nitrogen at the original concentrations, for 24 hours, and then harvested. These are designated the "minus-nitrate to plus-nitrate" plants, or series III. All cultures were carried out in duplicate.

ANALYTICAL METHODS

Total organic acids were estimated by a modification of the method of Pucher, Vickery, and Wakeman (11, 12). Difficulty was encountered in obtaining an end point in the electrometric titration. This was ascribed to the phosphoric acid extracted from the tissue. The sulfuric acid used in acidifying the tissue for the extraction also interfered and was included in the estimation (4). Oxalic acid was only 50 per cent titrated and had to be separately determined and then included in the total acid estimation.

To obviate these difficulties, the tissue was brought to pH 1.0 with nitric acid instead of the sulfuric acid as recommended by Pucher, Vickery, and Wakeman (11), and recourse was had to a method described by Van Slyke and Palmer (16). Although a few additional steps were necessary, the estimation was facilitated by resorting to a colorimetric titration.

After the removal of the ether, according to the method of Pucher *et al.* (11), the chlorophyll and other ether-extracted pigments were dispersed in the aqueous solution. These must be removed before a colorimetric titration can be made. In order to do this, 5 ml. of NH_4NO_3 was added to the aqueous organic acid extract, which was approximately 25 ml. This precipitated the dispersed chlorophyll. The extract was then filtered through two layers of filter paper in a conical funnel (Whatman #50 below, and Whatman #42 above), and made up to volume in a 100-cc. volumetric flask. The resulting solution was usually water-clear. Sometimes a faint yellow cast remained, however, which was presumed to be due to traces of the carotinoid pigments. This coloration was removed during the next step. That no loss in organic acids was occasioned by this procedure was shown by the results of electrometric titration before and after the removal of chlorophyll by this method, as indicated in figure 1.

Approximately 25 ml. of the cleared solution was shaken with 2 gm. of finely powdered $\text{Ca}(\text{OH})_2$ [see Van Slyke and Palmer (16)] for an hour. This step removed the remaining color and also the phosphates, sulfates, oxalates, and carbonates. The accuracy of the method was increased by removal of these ions previous to titration. The $\text{Ca}(\text{OH})_2$ suspension was passed through a dry, hard, quantitative filter paper without washing, and 10-ml. aliquots were titrated immediately.

The titrations were made in accordance with the procedure of Van Slyke and Palmer (16), using a 25-ml. volume and 2-ml. of 0.02 per cent tropeolin 00 as the indicator.

Malic, citric, and oxalic acids were determined by the methods of Pucher, Vickery, and Wakeman (12).

The estimation of ketonic acids was made by a modification of the method of Elliot, Benoy, and Baker (7). The modifications were similar to those of Donnelly (6). The bisulfite was added at a pH of 8, attained by bringing the solution to just above the phenolphthalein end point with NaOH. After standing 15 minutes, the solution was made acid with glacial acetic acid and the excess bisulfate was titrated. The bound bisulfite was then liberated with Na_2HPO_4 and titrated with standard iodine solution.

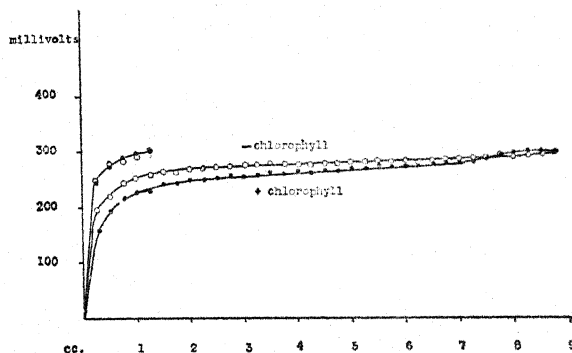


FIG. 1. ELECTROMETRIC TITRATION CURVES OF THE ORGANIC ACID EXTRACT BETWEEN pH 7.8 AND 2.6 WITH AND WITHOUT CHLOROPHYLL REMOVED

EXPERIMENTAL RESULTS

Total organic acids

The data presented are purely on a comparative basis, since the proper organic acid correction factor was not determined for oat tissue. This should not interfere with the proper interpretation of results obtained with any given species.

The data showing the variations in the organic acid content of tops and of roots within the various treatments were calculated in terms of milliequivalents per gram of dry tissue. The value per gram of dry tissue for each culture was multiplied by the dry weight of the culture, which gave the total milliequivalents of organic acid per culture. The values for the tops and roots were calculated separately and added together to give the total per culture. The absolute quantity of organic acids of the original culture was then subtracted from that of each treated culture to obtain the gain or loss of organic acids for each culture during the experimental period. The total gains or losses for tops plus roots were also calculated. The values representing the total organic acid content of oat tops, in milliequivalents per unit of dry tissue, were plotted against the

oxygen levels of the substrate as shown in figure 2. The corresponding data for roots were plotted in the same manner as were the data for tops and are shown in figure 3.

It will be observed from figures 2 and 3, that the oxygen tensions in the substrate exert a very marked influence on the type of metabolism of the plants. Low oxygen concentrations, 0 and 4 p.p.m., throw the plants into an anaerobic or at least a semianaerobic type of respiration, resulting in a high content of organic acids as a consequence of incomplete oxidation of sugars or other substrate material, as compared with the organic acid content of plants grown at the higher oxygen levels, within both the plus-nitrogen and the minus-nitrogen series. Conversely, the higher oxygen tensions produce an aerobic type of respiration, resulting in a much lower production of organic acids. This interpretation is based on the assumption that carbohydrates constitute the substrate being

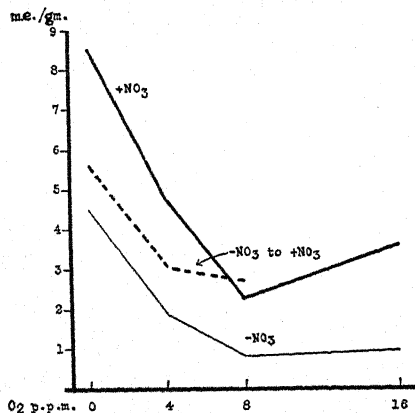


FIG. 2

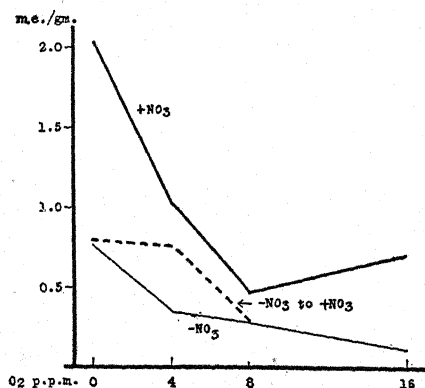


FIG. 3

FIG. 2. ORGANIC ACID CONTENT OF TOPS OF OAT PLANTS GROWN DURING AN EXPERIMENTAL INTERVAL OF 10 DAYS AT DIFFERENT OXYGEN LEVELS

FIG. 3. ORGANIC ACID CONTENT OF ROOTS OF OAT PLANTS GROWN DURING AN EXPERIMENTAL INTERVAL OF 10 DAYS AT DIFFERENT OXYGEN LEVELS

utilized, and therefore, the incomplete oxidation of these sugars will result in organic acids as end products of anaerobic respiration. All the data obtained point to the validity of this assumption, as does also the work by other investigators (17).

The expression of the data of organic acid content of the plants on the relative basis of milliequivalents per unit of dry tissue does not necessarily take into account either the material development of the plants in the different cultures or the absolute quantities of organic acids produced by them during the experimental period under the influence of the oxygen treatments. The absolute gain or loss of total organic acids during the experimental period was calculated, therefore, as above described, for the plants of each culture of the three series, to determine whether the relations between organic acid production and the effective oxygen levels of the substrate might show any serious discrepancies when judged by another criterion. The gains or losses, absolute totals for tops

plus roots, were plotted against the oxygen concentrations of the nutrient substrate, and are shown in figure 4. Comparison of the graphs in this figure with the corresponding graphs of figure 2 indicates that the important relationships brought out in connection with the graphs of figure 2 could apply here also. Further observation shows that the plants of the minus-nitrate cultures, series II, grown at the higher oxygen levels actually suffered a loss of a considerable portion of the organic acids produced and accumulated by the plants prior to the initiation of the experimental treatment period. This illustrates in a striking manner the determinative influence of an adequate oxygen supply in the nutrient substrate upon the organic acid metabolism in these plants.

Loehwing (10), working with sunflowers and soybeans growing in sand and in soil, also found an increase in the buffer capacity of nonaerated over aerated plants in the region of the buffer curve that would correspond to the organic

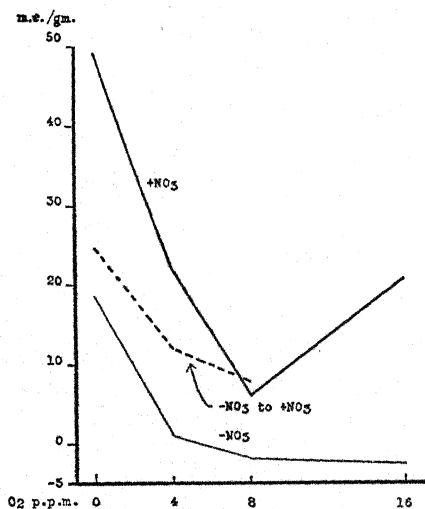


FIG. 4. NET GAIN OR LOSS OF TOTAL ORGANIC ACIDS OF OAT PLANTS GROWN DURING AN EXPERIMENTAL INTERVAL OF 10 DAYS AT DIFFERENT OXYGEN LEVELS

acids. Un-aerated sunflowers possessed a greater free acidity of the sap than did the aerated plants. This suggests a higher acid content in the nonaerated than in the aerated plants. Aerated roots were poorly buffered against acid and alkali with a steep gradient in the median portion of the buffer curves.

All of the data presented by Loehwing can be interpreted only to mean that organic acids accumulated to a greater extent in the unaerated than in the aerated plants. This is in accord with the data here presented.

On the other hand, Ulrich (15), working with decapitated roots, found that variations in the dissolved oxygen tension had no influence upon the organic acid production of the roots. In this connection it is important to point out that the shift from an aerobic to an anaerobic type of metabolism in a plant is a gradual process the full effectiveness of which becomes apparent only after a considerable interval of time and that this response varies from species to species.²

² Data presented by S. G. Gilbert in doctorate thesis, Rutgers University 1941

Influence of the nitrate ion

Nitrogen supplied in the culture solutions in the form of the nitrate ion exerted a pronounced influence on the organic acid production by the indicator plants in these studies. The plants of series II, which were grown without nitrogen in any form during the experimental period, showed a much lower content of total organic acid than did plants of the corresponding plus-nitrogen cultures of series I. This is clearly indicated in figure 2. The plants of the minus-nitrogen cultures, with the exception of those at the 0 oxygen level had a lower content of total organic acids than did the plants of the original cultures at the beginning of the experimental interval. At the higher oxygen levels (8 and 16 p.p.m.), as already pointed out, the plants of these cultures actually utilized, possibly as respiratory material, a portion of the organic acids accumulated prior to the initiation of the experimental treatment period. This is indicated by the data of gains and losses of total organic acids, represented by the graphs of figure 4, which thus emphasize the effectiveness not only of the oxygen concentration of the culture solution but also that of the nitrate ion in organic acid metabolism. When at the end of the experimental interval nitrate was supplied to the plants of the minus-nitrate cultures, the total organic acid content of the plants increased in 24 hours to a point intermediate between the values obtained for the plants of the plus-nitrate cultures and those of the minus-nitrate cultures of series I and II, respectively.

The quantitative data for the roots, presented in figure 3, indicate the same response to the influence of the nitrate ion as do the data for the tops. Thus, the nitrate ion appears to be specifically concerned with organic acid production. That the nitrate ion, and not nitrogen as such, is here involved is shown by comparison with the work of Clark (5), Wadleigh and Shive (20), and Blackman and Templeman (3). These investigators have found that plants grown with nitrogen supplied as ammonium always contained much less organic acids than did plants grown with nitrogen supplied as nitrate.

It is well known, of course, that the absorption of the ammonium ion by plants promotes the synthesis of amides, and since organic acids are the precursors of amides, this may account for the relatively low content of organic acids in plants grown with nitrogen supplied in the form of ammonium salts. This would explain also the relatively low content of organic acids in the minus-nitrogen plants of series II, if it is assumed that ammonium becomes available in these plants through hydrolytic or other plant processes in the absence of an external source of nitrogen.

Individual organic acids

Malic acid. When the data for malic acid (table 1) are examined it will be observed that although the content of this acid, in terms of milliequivalents per gram of dry tissue at the end of the experimental interval, is only about one half that at the beginning of the interval, there is actually an overall gain per culture, except in the plants of the minus-nitrate cultures at 0 and 4 p.p.m. of oxygen in the substrate. It will be observed also that in the plus-nitrate cultures the

oxygen level of the substrate exerted no apparent influence upon the accumulation of this acid in the plants. The plants of the minus-nitrate cultures grown at 0 and 4 p.p.m. oxygen levels suffered a slight loss of the malic acid produced and accumulated by the plants prior to the initiation of the experimental interval. The malic acid content of these plants, however, shows progressively higher values, in terms of milliequivalents per gram of tissue, with increasing oxygen tension of the substrate. This relationship between malic acid content and oxygen tension of the substrate is the direct opposite of that shown for all the other organic acids here considered, including the unknowns. The fact that these plants suffered a loss of malic acid at low oxygen tensions may be an indication that this acid is actually consumed in some anaerobic phase of metabolism. Genevois (8) has shown that similar responses occur in grapes. That

TABLE 1

Individual organic acid concentration of oat tops as influenced by the concentration of dissolved oxygen and form of nitrogen in the nutrient substrate

	O ₂ CONCENTRATION	MALIC ACID		OXALIC ACID		CARBOXYL ACIDS AS PYRUVIC ACID		UNKNOWN ORGANIC ACIDS	
		Per gram dry tissue	Gain or loss per culture	Per gram dry tissue	Gain or loss per culture	Per gram dry tissue	Gain or loss per culture	Per gram dry tissue	Gain or loss per culture
Original	p.p.m. Equilibrium with atmosphere	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
Plus-nitrate cultures, series I	0.0	0.758	+1.942	0.718	+4.786	0.076	+0.344	6.972	+41.38
	4.0	0.768	+2.042	0.714	+4.790	0.044	+0.125	3.254	+16.81
	8.0	0.728	+1.584	0.078	+0.512	0.073	+0.309	1.434	+4.05
	16.0	0.733	+2.643	0.000	-1.616	0.079	+0.479	2.915	+17.91
Minus-nitrate cultures, series II	0.0	0.310	-1.331	0.048	+0.293	0.182	+0.938	4.186	+20.11
	4.0	0.310	-1.584	0.012	+0.069	0.146	+0.599	1.598	+3.02
	8.0	0.491	+0.299	0.012	+0.101	0.125	+0.878	0.401	-2.04
	16.0	0.668	+1.158	0.032	+0.216	0.037	+0.425	0.260	-3.63

author found that malic acid was actually respired during semianaerobic conditions in the grape plant.

That the nitrate ion has a determinative effect upon malic acid production is clearly shown by the fact that the yield of this acid from the plus-nitrate plants is much higher than the corresponding yield from the minus-nitrate plants. The malic acid content of the plus-nitrate plants at low oxygen levels is more than double the content in the plants of the corresponding minus-nitrate cultures.

Oxalic acid. The production of oxalic acid presents a different situation from that of malic acid. In table 1 the usual inverse relationship is evident between the oxalic acid content of the plus-nitrate plants and oxygen concentration of the substrate. The minus-nitrate cultures have a very low content of oxalic acid, with no significant variation related to the oxygen tensions of the substrate.

The inevitable conclusion is that oxalic acid production is directly related to the presence of the nitrate ion and is inversely dependent on the oxygen concentration of the substrate. The connection between these two facts may be significant and suggests a direct association of oxalic acid production with nitrate reduction, since it has been shown (14) that nitrate reduction proceeds at a more rapid rate at low than at high oxygen levels in the substrate.

Carbonyl Acids. In an attempt to fractionate the organic acids further into characteristic types, the ketonic acids were determined as a group and expressed as pyruvic acid in terms of milliequivalents per gram of dry tissue. Only a small fraction of the total, however, was found to be due to these acids. No relationship of carbonyl acids with the oxygen concentration of the substrate is evident in the plants of the plus-nitrate cultures, although the content of these acids in the minus-nitrate plants shows a very definite inverse relation with oxygen levels. Furthermore, these are the only acids for which higher values are shown for the plants of the minus-nitrate, than for corresponding ones of the plus-nitrate, cultures. There is at present no explanation for this departure from the general trends of organic acid production as indicated by quantitative data.

Unknown organic acids. The unknown organic acids still represent the largest fraction of the total organic acids of the test plants here considered. No picture of the organic acid relationships in the metabolism of the plant will be complete until the components of this unknown fraction are separated and identified. It is this fraction which determines the general trends and dominates the overall picture of organic acid production.

SUMMARY

Determinations were made of the total organic acid content of oat plants grown at varying oxygen tensions of the nutrient substrates, with and without a supply of nitrogen in the form of nitrate.

The yield of total organic acids was invariably higher at low than at high oxygen levels in the substrate.

The yield of total organic acids was invariably higher in the plants of the plus nitrate than in those of the corresponding minus nitrate cultures. The higher yields of the former can be ascribed only to the presence of the nitrate ion.

The yield of malic acid was higher in the plants of the plus-nitrate than in those of the corresponding minus-nitrate cultures, but the oxygen levels of the substrate were without a significant effect upon the production of this acid in the plants of the plus-nitrate cultures. The malic acid content of the minus-nitrate plants, however, was lower at the low than at the high oxygen levels—a relationship directly opposite to that shown for all the other organic acids considered, including the unknown.

Oxalic acid production was largely dependent upon the presence of the nitrate ion and was inversely related to the oxygen tension of the substrate.

The carbonyl acids, determined as a group, were the only ones for which higher values were shown for minus-nitrate plants than for the corresponding plus-nitrate plants.

The unknown organic acids represented the largest fraction of the total organic acid content of the test plants, determined the general trends, and dominated the overall picture of organic acid production.

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SOIL-PLANT RELATIONS: I. THE QUANTITATIVE RELATION OF EXCHANGEABLE POTASSIUM TO CROP YIELDS AND TO CROP RESPONSE TO POTASH ADDITIONS¹

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The calculation of crop yields, of yield increases from fertilizer use, and of fertilizer requirements directly from simple chemical soil tests has been one of the main objectives of research in soil chemistry. The approximate achievement of these objectives for potash and phosphate soil tests has lately been realized in studies carried on at the Illinois Agricultural Experiment Station. This is the first paper in a series which will present the scientific aspects of the study. The practical application of the study is already being made through the extension soil-testing program in Illinois.

In general, the soils in the corn belt region of the United States are not considered to be potash-deficient. There are many areas within the Corn Belt, however, where soils highly deficient in potash are found. In the southern third of Illinois a high percentage of the soils are deficient in potash, as indicated by the results from the soil experiment fields and chemical studies in this region. These soils are strongly weathered and leached and have slow internal drainage because of heavy subsoils and poor structural development.

A generalized map of Illinois was prepared by the writer some years ago showing the areas where potash was seldom deficient, areas where such deficiencies were frequent, and still others where the soils were usually seriously deficient (4). Such a map is of value in showing the general situation throughout the state. It warns the farmers in the potash-deficient areas that they should inquire as to the possibility of potash need on their own farms, but it does not tell the farmer whether his own particular soil is deficient in potash, the extent of the deficiency, or the amount of potash fertilizer needed. The interpretation of experiment field results is also limited to generalizations because no one experiment field soil on one particular soil type can represent the varying potassium deficiencies to be found within that type or on other types. Areas of any given soil type may vary greatly with respect to their potassium deficiencies, partly because of natural variation and also as a result of the soil management previously practiced. The fertilizer requirement should vary correspondingly. Therefore, a knowledge of the soil type and of the response to potassium found by experiment field methods on one particular area of the type is not sufficient information to warrant a specific recommendation for potash use throughout that type. On the other hand, experiment field results are essential for this study, as will be shown by their use in this paper.

¹ Contribution from the department of agronomy, Agricultural Experiment Station, University of Illinois. Published with the approval of the director of the experiment station.

In 1932 the writer published a test for exchangeable potassium in soils (3) and correlated it with the response of the common field crops to potash fertilizers². This test measures the total exchangeable potassium in soils with approximately quantitative accuracy when the author's technics are followed. It has been found to be accurate for soils with base-exchange capacities ranging from less than 4 to about 40 m.e. per 100 gm. of soil (6, 14). This test has provided an easy and rapid means of determining the amounts of exchangeable potassium in farm soils, and its use is the first step in determining the potassium requirement. It has been widely used for this purpose, but its greatest possibilities have not heretofore been explored.

The study of exchangeable potassium and crop response to added potash reported in this paper reveals a good correlation between the amount of this form of potassium in corn belt soils and the increase in the yield of corn which is obtained when a potash fertilizer is used in adequate amounts. The significance of this fact in the scientific study of soil-plant relations is discussed, and it is shown that, through the use of the test for exchangeable potassium, estimations can now be made of (a) the potash deficiency on each farm soil, (b) the yield increase on each, (c) the potash requirements for the majority of corn belt soils, and (d) the economics of potash use.

EXPERIMENTAL

Soils studied and their treatment

The soils used were the surface soils of the RLP plots from 23 Illinois Experiment fields, which received crop residues and legume green manure (R), limestone (L), and phosphate (P) as their standard treatment. The crop yield data used in the study included the yields from the RLP and RLPK plots, the soil management and treatment systems of which were as follows (2):

A rotation of crops, usually a 4-year rotation of corn, oats, red clover or mixed hay, and wheat or corn, corn, oats, and wheat.

The growing of a green manure crop of sweet clover (R) turned under in the spring for corn.

The return of crop residues (R), cornstalks and grain straw, a practice which varied somewhat during the years when the return of straw was omitted from some fields during some periods.

The turning under of the last cutting of red clover or mixed hay (R).

The use of limestone (L) on all fields, in an attempt to maintain a reaction favorable for sweet clover and alfalfa growth.

The addition of large amounts of rock phosphate (P) over a period of years, most of the fields having received a total of 4 tons since they were started. (The Antioch and Bloomington fields originally received bone meal.)

The foregoing practices were common to the RLP and RLPK plots, and in addition the RLPK plot received 800 pounds of Kainit broadcast each 4-year rotation, 400 pounds ahead of the corn and 400 pounds ahead of the wheat. In 1932 this treatment was changed to KCl

² Bray, R. H., and DeTurk, E. E. The Illinois potash test. 1934. Ill. Agr. Exp. Sta. Agron. Dept. Pamphlet AG64. [Mimeographed.]

Bray, R. H. The chemical nature of soil potassium in relation to its availability in Illinois soils. 1940. [Unpublished doctor's thesis, University of Illinois, Urbana.]

(50 per cent K_2O), 100 pounds per acre hill-dropped for corn, 200 pounds broadcast for wheat, and 100 pounds broadcast for the legume. Since no significant increases are obtained when these amounts of KCl are doubled on the soils most deficient in potash, it is assumed that these treatments are adequate for maximum yields.

In this system the legumes and crop residues (R) are supposed to supply the nitrogen needed, and the limestone (L) supplies both calcium and magnesium, besides making the pH favorable for legume growth. No other elements are known to be deficient except boron, which is somewhat deficient for clovers, alfalfa, and lespedeza in some southern Illinois soils, especially in dry seasons. Exchangeable magnesium is also extremely low in some of the gray soils, although not yet recognized as being deficient.

The surface soils are mainly silt loams, silty clay loams, or silty clays, except for the Oquawka sandy soil. The silt loam fields vary greatly, especially in sub-surface drainage, organic matter content, colloidal clay content, and stage of maturity as shown by their weathered and leached condition. The silt loams in southern Illinois are mainly well weathered and leached and have gray silt loam surface soils and tight clay subsoils.

The colloidal clay of all of the soils used is principally of the beidellite-illite type (11). The total potassium content varies with the weathered status of the soil type (4), which in turn varies with the depth of loess and its distance from the source of loess (17). The parent material was mainly loess in the western and southern parts of the state and loess-like material in the north-eastern part. With respect to the kind of organic and inorganic materials and the range of amounts present, these soils represent the majority of the soils in the Corn Belt.

None of the limed soils were more than slightly acid, as shown by the glass electrode values run with a 1:1 soil-water ratio. Their degree of saturation with bases was correspondingly high.

The dates of starting the fields, the range of the base-exchange capacities, the pH values of the RLP plots, and the principal soil type represented on each field are given in table 1. The soil samples studies were taken³ during the 1935 season. Each sample was a composite of 20 samples from each RLP plot, making a total of 88 composite samples from the 23 experiment fields included in this study.

Method for determining exchangeable potassium

The exchangeable potassium was determined by soil test technics readily adaptable to large-scale testing programs, using the test originally described by the writer (3), but modified during the last 10 years as described below. After a thorough study of the various methods suggested for this purpose (6, 14), this method was chosen as quantitatively the most accurate.

The directions for the modified test are more fully described in University of Illinois mimeographed pamphlet AG 878⁴, but are recorded in some detail here because they have not been published in any of the scientific journals.

³ By F. C. Bauer, H. J. Snider, and other members of the agronomy staff.

⁴ Bray, R. H. The use of sodium perchlorate as a reagent for extracting the replaceable and water-soluble constituents in soils. 1936. Ill. Agr. Exp. Sta. Agron. Dept. Pamphlets AG424 and 878. [Mimeographed.]

Reagent A.—A neutral solution of approximately 22 per cent by weight of hydrated NaClO_4 in H_2O or a similar NaNO_3 solution.

TABLE 1
General soil data on RLP plots of Illinois experiment fields

EXPERIMENT FIELD	PRINCIPAL SOIL TYPE	BASE- EXCHANGE CAPACITY	pH RANGE ON RLP PLOTS 1935 SAMPLES	DATE OF START OF FIELD
		<i>m.e./100 gm.</i>		
Grouping 1—Brown to black silt and clay loams (least mature soils)				
Aledo.....	Sable silty clay	25-35	5.7-5.9	1910
Bloomington.....	Lisbon silty clay loam*	20-30†	5.7	1902
Dixon.....	Muscatine silt loam	20-30†	5.9-6.3	1910
Joliet.....	Swygert silt loam	27	5.7-6.2	1914
Kewanee.....	Muscatine silt loam*	20-30†	6.0-6.2	1915
Mt. Morris.....	Tama silt loam	26	6.4-6.6	1910
Grouping 2—Grayish brown silt loams (more mature soils)				
Carlinville.....	Ebbert silt loam*	18-25†	6.0-6.5	1910
Carthage.....	Herrick silt loam*	25	6.1-6.4	1911
Clayton.....	Oconee silt loam*	21	6.4-6.6	1911
Lebanon.....	Herrick silt loam	18-25†	5.8-6.5	1910
Grouping 3—Gray silt loams on tight clay (most ma- ture soils)				
Enfield.....	Loy silt loam*	8-12†	6.4-7.0	1913
Ewing.....	Cisne silt loam*	11	6.7-7.0	1910
Newton.....	Cisne silt loam*	8-12†	5.7-6.9	1912
Oblong.....	Rinard silt loam	8-12†	5.6-6.2	1912
Raleigh.....	Hoyleton silt loam*	8-12†	6.7-7.0	1910
Sparta.....	Bluford silt loam*	8-12†	6.0-6.6	1916
Toledo.....	Cisne silt loam	11	6.3-6.4	1913
Unionville.....	Not correlated	9	6.2-6.7	1911
Grouping 4—Miscellaneous				
Antioch.....	Miami silt loam*	10	6.7	1902
Elizabethtown.....	Not correlated—eroded	10-16	5.7-6.4	1918
Hartsburg.....	Sable silty clay	37	6.5-6.7	1912
Minonk.....	Saybrook silt loam*	37	6.3-6.8	1910
Oquawka.....	Loamy sand, not correlated	3-4	6.2-6.6	1914

* Mixed with relatively large areas of one or more associated types.

† Not determined—values given are the range for this soil type.

Reagent B.—Cobaltinitrite solution: 50 gm. of $\text{Co}(\text{NO}_3)_2$ and 300 gm. of NaNO_2 dissolved in water acidified with 25 ml. of acetic acid and made up to a liter with distilled water; allowed to stand 24 hours and filtered into a brown bottle.

Reagent C.—A 50-50 mixture by volume of synthetic methyl and isopropyl alcohols. The usual 95 per cent ethyl alcohol could be used in place of this mixture. Isopropyl alcohol can also be used but may require a different calibration from the 50-50 mixture.

Reagent D.—40 per cent formaldehyde.

Other materials.—Turbidity chart (a set of very thin black lines on bond paper); medicine droppers, calibrated in 0.1-ml. divisions; filter tubes; 5-gm. scoop.

Procedure.—Measure or, preferably, weigh 5 gms. of air-dry soil into an 18- by 100-mm. flat-bottomed vial containing 10 ml. of reagent A. Shake the vial for 1 minute and pour the contents on dry folded filter paper placed in a filter tube.

Measure 2 ml. of the filtrate into a 16.5- by 50-mm. flat-bottomed tube, add 4 drops of reagent D, and 6 drops (20 drops to 1 ml.) of reagent B, and shake. Add gently down the side of the tube 2 ml. of reagent C so that two layers are formed. Mix gently at first, then more rapidly until the two layers are mixed. Let the mixture stand 2 minutes. Take a clean 16.5- by 50-mm. flat-bottomed vial and place it on the turbidity chart which is on a glass platform and is illuminated from below by an enclosed 6-watt (120-volt) candelabra-base Mazda lamp. The whole device is covered so that no outside source of light interferes with the reading.

Using the calibrated medicine dropper, measure the suspension of developed precipitate into the vial until the thin black lines are just obscured. Be careful to fix the focus of the eye on the chart instead of on the top of the solution. The number of milliliters of the turbid solution necessary to obscure the thin lines is read from the conversion table in terms of pounds of K or K_2O an acre.

A conversion table is established by using standard potassium solutions, and the precipitation and reading method have quantitative accuracy. For workers having imperfect vision, the test can be calibrated in terms of the individual worker's eyesight. The test should be carried out between 18° and 25° C. and on soils which have been air-dry for 8 to 10 days.⁵ Standard K solutions are used as a check on the accuracy of the whole procedure. The turbidity of the solution can also be measured with a higher degree of accuracy by a photometer.

PRESENTATION OF THE DATA

The crop data given in table 2 were obtained from the records of the Illinois Soil Experiment Field Division⁶. Except for the Bloomington and Antioch fields, each value represents the 4-year average yield of corn obtained on the field. Since corn is grown each year, the yield from each RLP plot or each RLPK plot is represented in the average. On the Illinois Soil Experiment Fields the RLPK plot is adjacent to the RLP plot in almost every case, and therefore a minimum of influence from soil variation is present in this study.

⁵ Thoroughly air-dried soils are absolutely necessary. For certain soils, the required drying period may be longer than that indicated. Low values are obtained on soils not held long enough.

⁶ The writer is indebted to F. C. Bauer, in charge of the experiment fields, for the yield data used in this paper.

TABLE 2
*Corn yields on plots of Illinois experiment fields**

EXPERIMENT FIELD	ROTATION AVERAGES, IN BUSHELS PER ACRE						EXCHANGE- ABLE K OF RLP PLOTS
	1934-1937 Rotation			1938-1941 Rotation			
	RLP	RLPK	Increase for K	RLP	RLPK	Increase for K	
	(y)	(A)	(A - y)	(y)	(A)	(A - y)	lbs./A.
Grouping 1							
Aledo.....	72.7	74.0	1.3	99.8	104.5	4.7	322
Bloomington†.....				63.3	66.2	2.9	260
Dixon†.....	73.3	86.4	13.1	93.9	99.1	5.2	265
Joliet.....	39.1	40.0	0.9	63.3	69.4	6.1	212
Kewanee.....	70.6	68.8	-1.8	97.0	100.3	3.3	222
Mt. Morris.....	63.1	66.8	3.7	89.5	99.4	9.9	237
Grouping 2							
Carlinville.....	35.5	43.7	8.2	73.7	85.5	11.8	174
Carthage.....	46.3	48.2	1.9	91.0	93.9	2.9	241
Clayton.....	30.6	35.2	4.6	79.3	89.0	9.7	158
Lebanon.....	64.4	71.0	6.6	101.0	107.7	6.7	156
Grouping 3							
Enfield.....	24.3	38.4	14.1	39.9	60.2	20.3	76
Ewing.....	15.0	40.5	25.5	21.1	55.2	34.1	<50
Newton.....	12.3	28.8	16.5	33.8	54.1	20.3	86
Oblong.....	35.4	53.3	17.9	36.6	71.0	34.4	75
Raleigh.....	30.4	35.7	5.3	27.9	56.1	28.2	73
Sparta.....	14.7	19.7	5.0	27.0	45.9	18.9	66
Toledo.....	25.6	51.7	26.1	32.8	70.8	38.0	50
Unionville.....	25.1	29.7	4.6	132
Grouping 4							
Antioch†.....				35.9	44.5	8.6	123
Elizabethtown.....	32.8	31.6	-1.2	62.3	63.1	0.8	211
Hartsburg.....	61.6	58.2	-3.4	80.6	82.0	1.4	225
Minonk.....	66.7	65.9	-0.8	96.3	91.9	-4.4	219
Oquawka.....	34.3	36.0	1.7	49.9	53.7	3.8	90

* During the 1934-1937 rotation, mainly open-pollinated corn was grown, and several drouthy seasons occurred. During the 1938-1941 rotation, hybrid corn was grown except on the Toledo field, and in general the seasons were favorable.

† The Antioch and Bloomington fields grow corn only once every 4 years. The average used is for a longer period.

‡ The soil management practice was changed at Dixon during the periods included in this study.

The values for exchangeable potassium given in table 2 are the average for all the RLP plots on each field. In general the RLP plot values on any one field did not vary significantly.

The data in table 2 show that the response to added potash has varied greatly from field to field. Comparison of the increases with the exchangeable potassium

values shows that in general the largest increases were obtained from the fields having the lowest replaceable potassium content and *vice versa*.

ANALYSIS OF THE DATA

Correlation between exchangeable potassium content and increase in yield following potash use

An inspection of table 2 shows that there is only a fair correlation between the increase in corn yield obtained with potash fertilizers expressed in bushels per acre, and the total exchangeable potassium in the surface soil expressed in pounds per 2,000,000 pounds of soil.

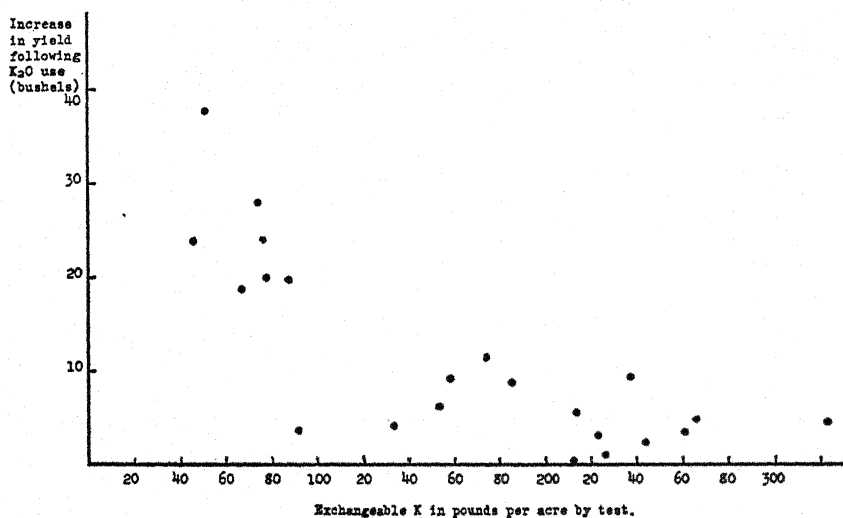


FIG. 1. RELATIONSHIP BETWEEN REPLACEABLE POTASSIUM AND INCREASES IN CORN YIELDS FOR K_2O USE

In figure 1 each dot represents the average increase in corn yield on one field for the 1938-1941 rotation period plotted against the average exchangeable potassium content. The dots exhibit considerable scattering, showing a general, but by no means close relation between the increase in yield expressed in bushels per acre and the exchangeable potassium content of the surface soil. An inspection of the yields on the RLP plots and their exchangeable potassium content likewise shows no exact relationship.

Correlation between exchangeable potassium and RLP yields expressed as percentage of RLPK yields

If, on the other hand, the RLP yields, expressed as percentages of the RLPK yields, are plotted against the exchangeable potassium, as in figure 2, a closer correlation is obtained. This shows that the exchangeable potassium values are directly related, not to the corn yield in bushels produced on any one field, but

to the *percentage yield* on the untreated soil where the yield on the soil adequately treated with K_2O is the 100 per cent yield, e.g.

$$\text{RLP plot yield} / \text{RLPK plot yield} \times 100 = \text{percentage yield without added potash}$$

The significance of this correlation becomes immediately obvious. One can now run a soil test for potassium and predict directly from the test value and the curve in figure 2 the percentage yield being obtained on that soil insofar as potash is concerned. This percentage yield value can also be described as the "percentage sufficiency of the available potassium," the "potassium fertility rating" of the soil; and the difference between it and 100 can be called the "percentage

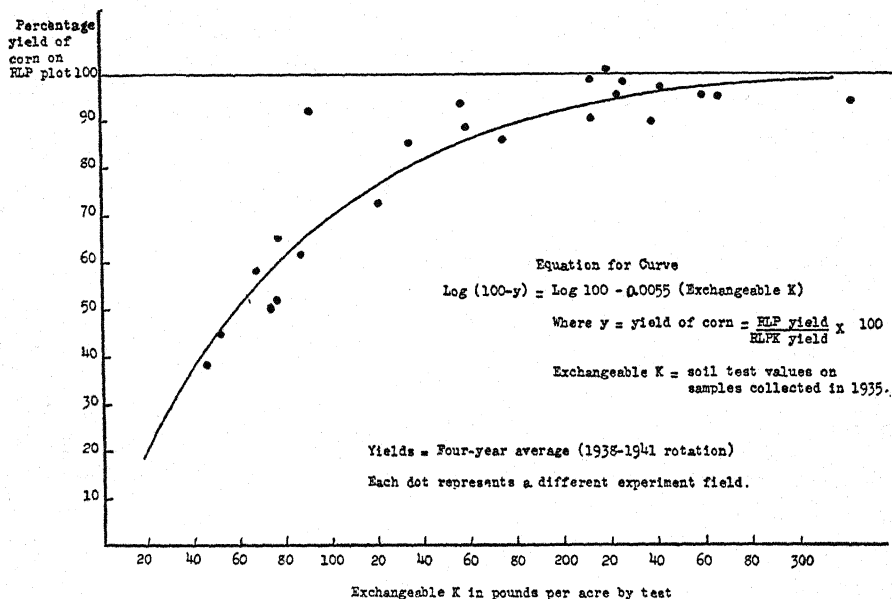


FIG. 2. RELATIONSHIP BETWEEN EXCHANGEABLE POTASSIUM AND CORN YIELDS ON UNTREATED PLOTS RECEIVING NO K_2O

deficiency in potassium." Since the exchangeable potassium value is related directly to the percentage yield obtained without added potash, it must also be related to the fertilizer requirement for potash.

A more convenient method of dealing with this relationship is through the equation for the curve. Since this resembled a typical "law of diminishing returns" curve, the Mitscherlich equation was applied as described below.

Application of Mitscherlich equation to data

The relationship between yield, added fertilizer, and the amount of the nutrient already present in the soil has been expressed by Mitscherlich through his "working equation" referred to as "the law of the soil," "law of physiological relations," and later as "the law of action of the growth factors."

Mitscherlich's equation is based on the assumption that "*the yield increases in proportion to the amount by which the current yield falls of the maximum yield, A*" (15,18).

$$\frac{dy}{dx} = (A - y)c \quad (1)$$

where y = yield, x = amount of nutrient added per amount of soil, A = maximum yield, and c = proportionality constant.

The integration of this equation is given by Mitscherlich (19) and leads to his "working equation" which is as follows:

$$\text{Log } (A - y) = \text{Log } A - c(x + b) \quad (2)$$

where A = maximum yield, y = yield obtained when x units of a nutrient are added to the soil, x = units of nutrient added per amount of soil, b = original nutrient content expressed in units of the added nutrient x , c = proportionality constant (Mitscherlich's "working factor").

Over a period of years Mitscherlich has shown, by continued experimentation, the general applicability of his law to many important factors, e.g., x and b in his equation. Furthermore, he has originated a special pot test technic for measuring the values in this equation.

Equation (2) expresses the nutrient content of the soil in terms of the fertilizer added, i.e., no direct determination of b was ever made by Mitscherlich, and c and b can be calculated only where x (the fertilizer) has been added to a sufficient number of different plots or pots in varying amounts.

Since only one rate, the maximum amount of KCl needed for the most deficient soils, or 400 pounds per rotation, has been used on all the Illinois experiment fields there are not sufficient data in the present study to apply equation (2).

To overcome this obstacle, the writer has modified equation (2) as follows:

$$\text{Log } (A - y) = \text{Log } A - c_1 b_1 \quad (3)$$

where c_1 = the proportionality constant, b_1 = the amount of nutrient in the surface soil *as measured by the soil test*, A = yield when potash is not deficient, y = yield when no potash is added.

The value of equation (3) lies in the fact that it eliminates the value x , or fertilizer added, and can be applied directly to the experiment field data as follows:

$$\text{Log (RLPK yield - RLP yield)} = \text{Log RLPK yield} - c_1 (\text{exchangeable K content}) \quad (3a)$$

Table 2 contains all the data necessary for the calculation of the c_1 values for the soils of all the soil experiment fields.

Another modification of the equation which includes x , or the amount of fertilizer, added is as follows:

$$\text{Log } (A - y) = \text{Log } A - (c_1 b_1 + cx) \quad (4)$$

where x = the amount of nutrient added, and c = proportionality constant of added nutrient. This equation is of value in connection with equation (3) in calculating fertilizer requirements on farm soils once c and c_1 have been determined and b_1 is measured directly on each field by the soil test.

To calculate the value of c_1 for the Illinois experiment field soils, values for A , y , and b_1 in equation (3) must be known. This involves certain assumptions with respect to the data in table 2. These are as follows:

The yield on each RLPK plot is the maximum yield of corn obtainable for that situation as far as potash is concerned, i.e., the potassium supply has been adequate and no further increases in yield would be obtained for additional increments of K_2O . Therefore, the RLPK plot yield = A in equation (3).

The difference in yield between the RLP plot and the RLPK plot is due entirely to the potash added, and is a measure of the effectiveness of the potassium in the RLP plot for corn growth. Therefore, the RLP plot yield = y in equation (3).

The total exchangeable potassium value as measured by the soil test is a measure of the amount of "available" potassium. Therefore, the test value = b_1 in equation (3).

Calculation of c_1 for the Illinois experiment field soils

The application of equation (3) to the crop response and chemical data in table 2 permits the calculation of c_1 for each experiment field.

According to table 2, the Enfield field during the 1938-1941 rotation grew 39.9 bushels of corn on the RLP plot, 60.2 on the RLPK plot and gave a soil test value on the RLP plot of 76 pounds of K per acre 2,000,000 pounds of soil. Substituting these values in equation (3) gives

$$\text{Log } (60.2 - 39.9) = \text{Log } 60.2 - c_1 \cdot 76$$

and solving for c_1 gives 0.0062 for the Enfield field.

Once the value of c_1 is known, the fertility rating or percentage yield of similar soils with respect to potassium can be approximately calculated from the soil test value. This can be done by the use of the percentage relationships. For example, with a soil testing 90 pounds,

$$\text{Log } (100 - y) = \text{Log } 100 - 0.0062 \cdot 90$$

Solving, gives $y = 72$ per cent, which means that a soil containing 90 pounds of exchangeable potassium can produce 72 per cent of the yield of corn possible where potassium is adequate; i.e. the yield, A , is used as the 100 per cent yield for this situation. In this example, the assumption involved in this calculation is that the second soil is similar to the Enfield soil except for the difference in exchangeable potassium.

The use of this percentage relationship in practice has possibilities for determining the fertility rating of the soil with respect to potassium. For example, where the c_1 value or values are known for a group of soils, the potassium fertility rating can be calculated for each particular soil by merely testing the soil and substituting the test value for b_1 in equation (3), using $A = 100$ (per cent). This will give y , or the yield without added K_2O , in terms of per cent, and this percentage value for y is the potassium fertility rating where 100 equals the

maximum rating with potassium supplied. The successful use of the soil test value for this purpose depends upon how nearly constant the c_1 values are for similar soils and whether or not c_1 values can be established for all soils.

TABLE 3

Soil test values for replaceable potassium on samples collected in 1935 from the Illinois experiment fields and the calculated average values for c_1 , for different rotation periods

EXPERIMENT FIELD	REPLACEABLE K IN LBS./A.	c_1 VALUES FOR DIFFERENT PERIODS	
		1934-1937	1938-1941
Grouping 1	(b_1)		
Aledo.....	322	.0055	.0041
Bloomington*.....	260		.0048
Dixon.....	265	.0031	.0048
Joliet.....	212		.0050
Kewanee.....	222		.0066
Mt. Morris.....	237	.0053	.0042
Average.....		.0047	.0050
Grouping 2			
Carlinville.....	174	.0042	.0049
Carthage.....	241	.0058	.0063
Clayton.....	158	.0056	.0061
Lebanon.....	156	.0066	.0077
Average.....		.0055	.0062
Grouping 3			
Enfield.....	76	.0044	.0062
Ewing.....	<50	.0039	.0040
Newton.....	86	.0028	.0050
Oblong.....	75	.0063	.0042
Raleigh.....	73	.0113	.0041
Sparta.....	66	.0090	.0058
Toledo.....	50	.0060	.0054
Unionville.....	132	.0061	
Average.....		.0062	.0050
Grouping 4			
Antioch*.....	123		.0058
Elizabethtown.....	211		.0090
Hartsburg.....	225		.0079
Minonk.....	219		
Oquawka.....	90	.0147	.0120

* Includes a longer rotation period.

Table 3 gives the values for c_1 calculated as illustrated above. Two rotation periods, 1934-1937 and 1938-1941, are included. The exchangeable potassium values (b_1) are the amounts found in the 1935 samples.

The first rotation period covers the period closest to the sampling date. From this standpoint, it should give the most accurate c_1 values, because any decrease in exchangeable potassium, as would be expected over a period of years, should influence the 1938-1941 values for c_1 the more. Fields in group 3 do show some decline in the c_1 value for the latter period, but groups 1 and 2 give no evidence that any significant decrease in exchangeable potassium has occurred. The average c_1 value for all three groups during both periods is 0.0055. This indicates that any expected change in exchangeable potassium has not been great enough to interfere with the calculation of an average c_1 value for practical use. Other studies also show that changes have not been great. Although the exchangeable potassium may not have changed significantly in these soils, which are apparently in equilibrium with the cropping system used, this cannot be construed as indicating that under other conditions this will also hold. Soils may vary rapidly in their exchangeable potassium when the cropping system or soil treatments are altered. This should not, of course, change the value of c_1 , but it will affect the period of time over which predictions from a soil test value will be of use. Though the possibility of long range predictions is indicated, when the soil tested is a relatively untreated soil, i.e., has not been built up significantly by potash additions, interpretations for soils already treated with potash may in some cases be good for only the following crop year.

Group 4 averages considerably higher than 0.0055. In this group the Hartsburg and Minonk fields have rather consistently give decreased yields for potash use and would not be expected to give a reliable c_1 value. The Elizabethtown field also gave decreases for potash use during the more drouthy period. Of the remaining two fields, which give fairly low test values, the Antioch field c_1 value of 0.0058 is nearly the same as the average for the other fields, but the especially drouthy Oquawka sand gives a c_1 value entirely out of line.⁷

Theoretically, equation (3) should be applied to the individual yield values, not to average values. The value of c_1 could be expected to vary somewhat for different seasonal conditions. In calculating the c_1 values for use in practice, however, the rotation averages are used, and c_1 is a value for average seasonal conditions.

Calculation of the percentage sufficiency of exchangeable potassium

An average c_1 value for corn, as calculated above, will be of little practical use if the deviations from the average are large. The test of the usefulness of an average c_1 value lies in the ability to calculate through its use values for either percentage sufficiency (percentage yield or potassium fertility rating) or yield increases in bushels per acre. Good general discussions of this type of application of Mitscherlich's law are given by Spillman and Lang (18) Olsen and Shaw (16), Briggs (10), Balmukand (1) and especially by Willcox (19).

The percentage sufficiency can be calculated directly from the soil test value without any additional information except the value for c_1 .

⁷ A preliminary study of the responses of the other crops on this field shows the c_1 value to be more in line with the results from other fields. Apparently the drouthy condition of this soil influences only the c_1 value for corn.

The yield increase in bushels per acre can be calculated only where either the yield without potash or the yield with adequate potash is known. In table 4

TABLE 4

Calculation of percentage sufficiency of soil potassium and of yield increases due to added potash on Illinois experiment fields

EXPERIMENT FIELD	EXCHANGEABLE K	RLP PLOT PERCENTAGE SUFFICIENCY 1938-1941*		RLPK PLOT YIELD INCREASE IN BUSHELS 1938-1941	
		Calculated†	Found	Calculated†	Found
	lbs./A.				
Grouping 1					
Aledo.....	322	98	94	1	5
Bloomington.....	260	96	96	2	3
Dixon.....	265	96	95	4	5
Joliet.....	212	93	91	5	6
Kewanee.....	222	94	96	6	3
Mt. Morris.....	237	95	90	4	10
Grouping 2					
Carlinville.....	174	89	86	9	12
Carthage.....	241	95	97	5	3
Clayton.....	158	86	89	11	10
Lebanon.....	156	86	94	16	7
Grouping 3					
Enfield.....	76	62	66	24	20
Ewing.....	<50	46	38	25	34
Newton.....	86	66	62	17	20
Oblong.....	75	62	52	22	34
Raleigh.....	73	59	50	19	28
Sparta.....	66	56	59	21	19
Toledo.....	50	46	46	38	38
Unionville.....	132	80	86	6	5
Grouping 4					
Antioch.....	123	78	81	10	8
Elizabethtown.....	211	93	99	5	1
Hartsburg.....	225	94	98	5	1
Minonk.....	219	94	102	6	-4
Oquawka.....	90	67	93	25	4

* Except for Bloomington, Antioch, and Unionville fields.

† Calculated from the following equations:

$$\text{Log } (100 - y) = \text{Log } 100 - 0.0055 (\text{exchangeable K})$$

where y = percentage sufficiency of soil K or the percentage yield obtainable on the RLP plot.

$$\text{Log } (A - \text{RLP plot yield}) = \text{Log } A - 0.0055 (\text{exchangeable K})$$

where A = yield in bushels obtainable on the RLPK plot.

the RLP plot yield was taken as the base and the RLPK plot yield was calculated in order to obtain the difference between them, or the calculated yield increase.

Table 4 gives the calculated and experimental values for both percentage

sufficiency and yield increase. Only the Oquawka sand field failed to give sufficient agreement between experimental and calculated values to permit the use of the average c_1 value for this crop-soil climate relation. The other 22 fields showed good agreement, as proved by the fact that the standard error of estimate is ± 5 per cent.

In equation (3) the soil test value is substituted for b_1 . This use of the soil test differs from that described by Willcox (19, chap. VIII). Willcox's suggested use is based on the unstated assumption that the soil nutrient measured by the soil test is present in the soil in the same form and possessing the same "availability" as the fertilizer form of the nutrient when it is first added. This is an assumption unsupported by any evidence, but it does represent a practical although not exact method of applying the Mitscherlich equation and constants to soil testing in lieu of any more scientific approach. The writer's application of the Mitscherlich equation, as given by equation (3), is not based on any such assumptions or use of the Mitscherlich constants. The constant c_1 is directly calculated from soil test and experiment field data for the soils and crops concerned, and this study has been preceded by other studies as to the quantitateness of the soil test, the nature of exchangeable potassium and its renewal from other forms, and numerous other phases of the chemistry of soil potash (8, 9, 11). Attention should also be directed to the fact that the Mitscherlich equation is used in this study because it fits the data, which is a different situation from that in which isolated data are interpreted through the Mitscherlich equation and constants, simply by assuming that these apply. The Mitscherlich equation is used because it is a convenient way of expressing the relation found between the exchangeable potassium and the crop growth and response, as shown by figure 2. The practical use of the potassium test is accompanied by tests for limestone and phosphate needs, and in practice any potash recommendation will be accompanied by recommendations for any other limiting nutrients. Thus the question as to whether or not c_1 remains a constant under conditions where other nutrients vary in their degree of deficiency does not enter the picture as far as the practical use of the test is concerned. It should also be mentioned that the application of the Mitscherlich equation, as made in this study, depends upon the ability of the soil test to give a quantitative measure of the exchangeable potassium. Many of the soil tests now in use cannot measure exchangeable potassium quantitatively, and hence the practical interpretations given in this paper cannot be made following their use (6, 15).

PRACTICAL APPLICATION

Variations in factors influencing crop growth

The data in table 2 for corn yields and responses to added potash were obtained on soils varying widely in their physical nature and in their yield under full treatment. These differences have produced no wider differences in the c_1 values between groups 1, 2, and 3 than occur within each group. From this standpoint, therefore, it is practical to use an average c_1 value for all the soils represented in these groups. This value, then, applies to all the corn belt

soils of similar physical and chemical nature and will include most of the timber and prairie soils in the Corn Belt.

Theoretically, variations in such properties as the magnitude of the base-exchange capacity will vary the effectiveness of the exchangeable potassium, as will also variations in nitrate production, CO_2 evolution, and the rate of renewal of the exchangeable potassium from nonexchangeable or difficultly exchangeable forms. Actually these variations, although represented on the field studies (5, 8, 9), have not resulted in too widely different c_1 values.

There is another group of factors which must also be considered. The average c_1 value of 0.0055 for corn was obtained under conditions where other nutrients were supposedly not deficient. Does this c_1 value hold in a practical way only for such soils, or will it hold for soils deficient in other nutrients? Baule's interpretation of Mitscherlich's data maintains that it will. This is in direct contrast to the old theory of "the limiting factor" (18). The Mitscherlich-Baule interpretations consider this older theory as thoroughly discredited. The fact that similar c_1 values are found for exchangeable potassium on soils varying widely in productivity under full treatment supports the Mitscherlich-Baule interpretation. In its fullest sense, this interpretation states that the variation in yield caused by varying a growth factor will follow the Mitscherlich equation regardless of the deficiencies or sufficiencies of the other factors.

If this is a fact, then the c_1 value for exchangeable potassium can be used to calculate yield responses on soils varying widely in their supplies of "available" phosphorus, nitrogen, calcium, magnesium, and other nutrients. This would mean that a soil 50 per cent deficient in potassium would give a double yield when adequate potash is applied, regardless of the supplies of the other nutrients. It means that, without potash, the other nutrients, regardless of the status of their deficiencies, are not being used efficiently. It means further that on potash-deficient soils added potash can produce increased yields by increasing the overall efficiency of the plant in obtaining and utilizing water and other nutrient elements which may or may not be deficient. And finally it means that an average c_1 value can be used in practice for most of the soils of the Corn Belt to calculate the present deficiency of a farmer's soil directly from a soil test value without knowledge of the past history of treatment, management, or deficiencies in other nutrients.

This seems to be too broad an interpretation to accept without some limitations. Though it appears to be true for the soil conditions usually found in the Corn Belt, theoretically certain conditions could be expected to make the use of c_1 less reliable.

A certain type of rainfall distribution encouraging luxuriant growth followed by hot winds and dry weather may cause (and has caused) decreases in yields on treated plots compared to the check plot yields where deficiencies are present. Soil factors which can change as rapidly as water and nitrate may often result in a smaller increase than expected, when potash is used on a potash-deficient soil, or may even result in a decrease in the total yield. This effect for silt and clay loam soils is already included, however, in the average c_1 value, which includes the results from more than one season. The fact that the Oquawka data do not

give a c_1 value for corn close to the average may be due to the drouthy nature of the sand found on this field.

It is to be expected that the equations under consideration and the Mitscherlich-Baule interpretations might fail at an extremely high productive capacity, as, for example, 300 bushels of corn an acre. It should be remembered that most, if not all, of the mathematical interpretations of natural laws, as in physics and and biology, apply only in the middle portion of the total range of conditions and fail at the extremes. This is equivalent to saying that new c_1 values would probable have to be computed from actual yields for extremely high yields of say more than 175 bushels, and that probably no equations would hold for yields of less than 15 to 20 bushels of corn an acre.

There are numerous experiment field data showing that where a soil is deficient in more than one nutrient, the addition of just one of them will bring about an increase in yield. In table 5 are given data for potash response on the same

TABLE 5
Response of corn to KCl on Ewing field
Average yields of 13 corn crops, in bushels per acre, up to 1941

ORIGINAL TREATMENT	YIELDS WITHOUT KCl	YIELDS WITH KCl	PERCENTAGE K SUFFICIENCY§
	(c)	(b)	
O.....	11.4	15.8*	73
R.....	13.6	34.3*	40
RL.....	16.3	38.4*	42
RLP.....	19.0	39.9*	48
RLP.....	19.0	46.5†	41
RLP.....	19.0	46.6‡	41

* New KCl across old treatments (original amounts).

† Old K treatment continued.

‡ New K across old K treatment (double K).

§ $\frac{\text{Yield without K}}{\text{Yield with K}} \times 100 = \text{percentage sufficiency.}$

field from differently treated plots. In all but one case, the percentage increase in yield is similar, showing that the Baule interpretation of Mitscherlich's data is applicable. This is only one of several similar sets of data, which confirm this relationship, obtained by Bauer in special studies. It appears, therefore, that it will not be necessary to restrict the interpretation of the data to soils where no nutrient but potash is deficient.

For the present, however, the writer is restricting the interpretation to cases where only the relatively immobile nutrients vary in their deficiencies. This eliminates water and nitrogen present as nitrate. Also the interpretation will be limited for the present to the silt loam and clay loam soils of the Corn Belt. This eliminates sands, peats, mucks, and alkali spots.

Applying soil testing to the individual farm soil

The fact that the exchangeable potassium is a measure of the percentage sufficiency of the soil potassium and the further fact that this relationship does

not change appreciably for the range of productivity now found in corn belt soils is of great practical significance to corn belt farmers.

As a result of knowing the c_1 value, established by the correlation between yield increases on the experiment fields and the soil test results, it is now possible to test each farmer's soil and estimate in a practical way the fertility rating with

TABLE 6
Economics of use of potash for corn
Results per acre

EXCHANGEABLE K	PERCENTAGE YIELD* OBTAIN- ABLE WITHOUT K ₂ O	AVERAGE YIELD IN PAST WITHOUT K ₂ O	AVERAGE YIELD IN FUTURE WITH K ₂ O	INCREASE FOR ADDED K ₂ O	K ₂ O NEEDED†	K ₂ O COST AS KCl
<i>lbs.</i>		<i>bu.</i>	<i>bu.</i>	<i>bu.</i>	<i>lbs.</i>	\$
55	53	20	38	18	72	3.60
		30	56	26		
		40	75	35		
		50	94	44		
73	63	20	32	12	65	3.25
		30	47	17		
		40	63	23		
		60	95	35		
95	74	20	27	7	56	2.80
		40	54	14		
		60	81	21		
		80	108	28		
127	84	20	24	4	43	2.15
		40	47	7		
		70	83	13		
		100	119	19		
150	90	20	22	2	34	1.70
		40	44	4		
		70	78	8		
		110	122	12		

* The percentage yield used in this practical application is based on 95 per cent as the maximum yield which can be most economically attained. Therefore $A = 95$ per cent in this use of the data.

† This is the K₂O requirement where other crops in the rotation are also being treated with potash salts according to their respective requirements.

respect to potash, the percentage yield increase which will be obtained as a result of applying adequate amounts of potash, the yield increase in bushels, based on the average yields in the recent past, and, when c is established for potash salts, the potash requirement.

A tentative value for c for KCl has been worked out by the writer. The K₂O requirements calculated by means of this value are included in table 6 in order

to illustrate the use of soil testing as it can now be applied to each farm soil in the Corn Belt, subject to the limitations already mentioned.

The first problem with respect to potash is — is it needed? The first steps in the solution of this problem are the correct sampling of the soil, its proper drying for a sufficiently long period and preparation for testing, and its testing by a method which measures the total exchangeable potassium. Next comes the interpretation of the test values in terms of the percentage sufficiency for the crop to be grown and the probable average increase in yield which can be expected, based on past yield performances. Following this, comes the estimation of the amount of K_2O needed, its cost, and the probable value of the increased yields.

Table 6 illustrates the use of this procedure. To apply the data in table 6 to a specific farm soil it is necessary to have the soil tested for exchangeable potassium and opposite this value in column 1, select, in column 3, the approximate average yield obtained on this field in the past. Column 5 gives the estimated average increase in yield for potash use in the future, and column 7 gives the cost of the added K_2O . All that remains to be done is to decide whether or not the expected increase will be of sufficient value to make the use of potash worth while.

This procedure represents the broadest use of the soil test value for exchangeable potassium and should be qualified insofar as possible by a knowledge of local conditions. It is a table to be used, not blindly, as has too often been the case with soil tests in the past, but with good judgment as to physical soil conditions, the probable deficiencies in other nutrients, and other factors influencing both yield and crop value, especially those not represented in field experiments on which this study was made.

Potassium requirements of other crops

Studies similar to the one reported in this paper have been made for mixed legumes, wheat, oats, and soybeans.

These studies do not support the original conclusion of Mitscherlich that all crops have the same c_1 value. The tentative values of c_1 for these crops are as follows: 0.0055 for mixed legumes, 0.012 for wheat in southern Illinois, 0.012 for oats, 0.0077 for soybeans. For the northern two thirds of Illinois, the values for c_1 for wheat are lower than 0.012, but the response to potash is low in this region making for a less accurate calculation of c_1 . This may or may not be the principal reason for the variation. These c_1 values are in line with what is already known about the relative potash needs of these crops.⁸

Phosphorus requirement of crops

Studies similar to that reported in this paper have been made, using the writer's new soil test for phosphorus⁹. This test employs 0.03 N NH_4F in

⁸ When the combined response to both P and K is calculated, a value of 0.0065 for corn for the soils in group 3, rather than 0.0055, appears to give the best agreement.

⁹ Bray, R. H. Rapid tests for measuring and differentiating between the adsorbed and acid-soluble forms of phosphate in soils. 1942. Ill. Agr. Exp. Sta. Agron. Dept. Pamphlet AG1028. [Mimeographed.]

0.1 N HCl as an extracting solution for soil phosphorus. The results of this investigation are not reported here, but it may be mentioned at this time that specific c_1 values for phosphorus for corn, legumes, and wheat have been established, proving that this soil test is measuring in a practical way the forms of phosphorus that are of most significance to plant growth (7). The deviations of the individual c_1 values from the average are, however, somewhat larger than with the potassium test.

CONCLUSIONS

The amount of exchangeable potassium in the surface soils of the Corn Belt is directly related to the ability of the soil to supply potassium to crops. This relationship can be expressed by the modified Mitscherlich equation as follows:

$$\text{Log } (A - y) = \text{Log } A - c_1 b_1$$

where A = yield in bushels when K is not deficient, y = yield obtained when b_1 = amount of exchangeable K in surface soil and c_1 = proportionality constant.

The above relationship holds with approximately the same value for c_1 where many physical and chemical soil properties vary within a rather wide range and where the ultimate yields under full treatment also vary considerably.

The soil test for exchangeable potassium described in this paper measures the total exchangeable potassium with the accuracy necessary to establish the above relationship

Through the medium of soil testing the above relationship can be applied in a practical way to each farm field for the solution of the following problems:

- (a) Is potash needed?
- (b) What is the approximate magnitude of the deficiency and the percentage yield being obtained without added potash?
- (c) Approximately how much will crop yields be increased by the use of adequate amounts of potash?
- (d) What is the approximate potash requirement?

The values of c_1 obtained for corn, legumes, soybeans, and wheat do not confirm Mitscherlich's original idea of a constant c value for all crops.

The more exact application of the results of this study to the solution of practical problems should, for the present, be limited to the soil conditions represented in the present investigation. These conditions apply to the great majority of the soils in the Corn Belt.

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DETERMINATION OF CERTAIN PHYSICAL PROPERTIES OF FOREST SOILS: II: METHODS UTILIZING LOOSE SAMPLES COLLECTED FROM PITS

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In stony soils, sampling with metal cylinders is commonly impractical if not impossible. When the cutting edge of a cylinder being driven into the soil encounters rocks about 5 or more cm. in diameter the cylinder is usually damaged and the sample has to be discarded. Even if the rock is only about 1.5 to 2.5 cm. in diameter the cylinder is likely to be damaged and the rock is either pushed outward, leaving a void in the sample, or pushed inward, compressing the sample. Consideration of these difficulties, which are frequently met in forest soils, led the writer to seek a technique by which pore volume, air capacity, field capacity, and volume weight could be measured without the use of metal cylinders. A procedure has been developed which meets this objective.

On analysis of the problem, it became clear that the two principal requirements to be met were: first, a method for determining the volume which the soil sample occupied in the field, that is, the volume of the soil in place; and second, a method for determining the absolute volume of soil material in large samples.

It has been found that the first of the foregoing requirements can be met by measuring the volume of a plaster of paris cast of the pit or cavity from which the sample was collected. Several other techniques for measuring the volume of soil pits are described in the literature. These include filling the pit with a measured volume of sand (3) or highly viscous fluid (1) and insertion of a thin-walled rubber bag which is filled with a measured volume of water (4). It is also possible that, following chemical treatment to render the walls impermeable, the volume of the pit can be determined by filling with water directly. Perhaps some of these methods will prove equally accurate and less time-consuming than the plaster of paris cast technique.

The second requirement is satisfied by measuring the volume of soil material of the entire sample in a large pycnometer, following evacuation, as described in an earlier paper by the writer (5).

It is essential that the soil be at its field capacity when sampled. This moisture content has been defined by Veihmeyer and Hendrickson (7) as "...the amount of water held in the soil after excess gravitational water has drained away and after the rate of downward movement of water has materially decreased ...". These authors concluded that "...there is a rather definite soil-moisture content which if measured within 2 or 3 days after a rain or an irrigation may be assumed to be the field capacity, if there are no discontinuities in structure or texture present and in the absence of a water table." This view that the field capacity represents a rather definite soil-moisture content is confirmed by the fact that various workers have found a relationship between field capacity and moisture

equivalent (2, 6, 7). The length of time required for soil water to attain the energy level referred to as the "field capacity" varies in different soils. The period allowed for drainage is usually 1 to 5 days; coarse-textured soils drain to their field capacity more quickly than do fine-textured soils. For practical purposes it may be assumed that a soil has reached its field capacity when samples taken 8 to 12 hours apart, following a prolonged rain or irrigation, show essentially the same moisture content.

It is recognized that a soil moisture content somewhat above or below field capacity at the time of sampling will cause errors in the results for both field capacity and air capacity. Values for volume weight, pore volume, and specific gravity, however, will not be affected. The advantages of sampling soils at field capacity are believed to outweigh the disadvantages. In fine-textured soils where substantial changes in volume accompany changes in moisture content, one obtains more satisfactory values for volume weight if the soils are allowed to expand in the field prior to sampling. Of even greater importance is the fact that field capacity is a *field value*, representing the moisture held by a soil when allowed to drain under natural conditions. This is of particular significance to the plant ecologist.

FIELD PROCEDURE

Points where sampling is to be carried on are established at random. As the soil must be at its field capacity when sampled, it is necessary either to await natural occurrence of this condition or to bring the soil to its field capacity by irrigation. In the latter case the spots where samples are to be taken may be covered with a layer of moist organic debris (leaves or needles) or other material to prevent excessive evaporation from the mineral soil surface. It also seems to be good practice to sever the tree roots entering the spot so that removal of moisture by transpiration is avoided. This may be accomplished with a sharp spade without any disturbance of the soil at the center of the spot where the samples are to be taken. The area of the square or circular plot thus treated may be about 8 to 10 square feet. With the soil at field capacity the actual sampling is undertaken. The detailed procedure follows:

The top of the soil horizon to be investigated is exposed, and a loose sample is removed with a knife, small trowel, or large spoon, leaving a pit. Immediately after removal, the soil sample is weighed in the field or placed in an air-tight container, which is returned to the laboratory for weighing. The object is to establish the weight of the sample at its field capacity. In removing the sample the bottom and side walls of the pit should be as little disturbed as possible. Roots should be cut off, not pulled out. Stones in the side walls or bottom are included in the sample if more than half their volume falls inside the pit boundaries, otherwise they are excluded from the sample, being left in place. Although dimensions of the pit will vary in accordance with the thickness of the horizon being investigated, a volume of about 1,000 to 2,000 cc. is recommended. Square or cylindrical pits are most convenient, but shape is not an important consideration; side walls should be maintained as nearly vertical as is convenient.

The natural tendency to make the pit wider at the top than at the bottom should be avoided.

Plaster of paris is then mixed with water and poured into the pit in order to obtain a cast. For good results the plaster of paris should flow readily; with experience the proper consistency is easily recognized. After $\frac{1}{2}$ to 1 hour is allowed for setting, the cast is excavated and wrapped in newspapers for transport to the laboratory. Final cleaning of soil from the surfaces is best accomplished in the laboratory after the casts have dried for one or more days.

The loose soil sample (after its weight at field capacity has been obtained) and the cast may be stored until the end of the field season, or the determinations may be made at once.

LABORATORY PROCEDURE

The volume of the cast, and consequently the volume of the soil in place, may be determined by one of two methods. The first necessitates thorough drying of the cast, after which it is weighed and coated with paraffin. Reweighing after coating permits calculation of the weight of paraffin added. The volume of the paraffin-coated cast is then determined in a large pycnometer. After allowance is made for the volume of paraffin added, the volume of the cast can be computed. A difficulty frequently encountered in this technique is that of obtaining a perfect coating of paraffin over the cast. The second method, which is the one favored by the writer, eliminates the need for coating the cast. The cast is permitted to stand in water for about 12 hours, after which it is evacuated for about an hour in a vacuum equal to 15 inches of mercury. It is then weighed in air and in water; with these data the volume is readily calculated.

The entire soil sample is oven-dried and the weight established. *Field capacity* in percentage of volume is obtained as follows:

Weight of sample at field capacity, gm.

$$\frac{\text{— weight of sample, oven-dry, gm.}}{\text{Volume of cast, cc.}} \times 100$$

Volume weight is equivalent to:

$$\frac{\text{Weight of sample, oven-dry, gm.}}{\text{Volume of cast, cc.}}$$

The entire soil sample is allowed to soak in water, with occasional stirring, for 24 to 48 hours. It is then transferred to a desiccator 8 inches in diameter with a tubulated cover and subjected to a vacuum equal to 15 inches of mercury for 2 to 3 hours with occasional shaking. The volume of the sample is then determined in a large pycnometer, as described in an earlier paper by the writer (5).

Pore volume (percentage) is computed as follows:

Volume of soil in place, cc.

$$\frac{\text{— volume of water displaced by entire soil sample, cc.}}{\text{Volume of soil in place, cc.}} \times 100$$

Air capacity (percentage) is equivalent to:

$$\frac{\text{Pore volume, cc.} - \text{moisture content of soil at field capacity, gm.}}{\text{Volume of soil in place, cc.}} \times 100$$

Specific gravity of the soil material is equivalent to:

$$\frac{\text{Oven-dry weight of soil, gm.}}{\text{Volume of water displaced by entire soil sample, cc.}}$$

COMPARISON OF RESULTS OBTAINED WITH AND WITHOUT USE OF METAL CYLINDERS

Two sets of comparisons of values obtained with and without use of metal cylinders are presented. The first concerns values for cylinder samples investigated according to the procedure referred to as "schedule A" and values obtained by the pit method. The second concerns values for cylinder samples examined according to the procedure referred to as "schedule B" and values obtained by the pit method.

The principal difference between schedule A and schedule B is the method employed in removing air from the soil sample. In schedule A air is removed by placing the cylinder sample in a tank and then gradually raising the water level to the top of the cylinder, where it is allowed to stand for 24 to 48 hours. Complete removal of air by this technique is impossible. In schedule B removal of air is accomplished by subjecting the soil sample to a vacuum equal to 15 inches of mercury for 2 to 3 hours. Details of these procedures are given in an earlier paper by the author (5).

Cylinder method (schedule A) vs. pit method

Volume weight. Volume weight values by the two methods should be in agreement, provided the volume of the soil in place has been accurately determined from the plaster of paris cast.

In table 1 are presented volume weight values for Merrimac sandy loam obtained from twelve stations in the Yale forest near Keene, New Hampshire. The samples represent the A horizon and were taken from the upper 10 cm. of mineral soil. Volume weight determined by the pit method averaged 0.005 ± 0.026 lower than by the cylinder method; this difference is not statistically significant. In another comparison involving Merrimac sand obtained from nine stations near New Haven, Connecticut, volume weight by the pit method averaged 0.023 ± 0.015 lower than by the cylinder method. In this case, too, the difference is not significant. Berlin clay loam obtained in the Eli Whitney forest, near New Haven, was used in a further comparison of the two methods. This soil was less uniform than Merrimac sandy loam and Merrimac sand. Twelve independent samples were examined by each method. Volume weight by the pit method averaged 0.838 ± 0.010 and by the cylinder method 0.863 ± 0.011 ; the difference of 0.025 is not significant. These values indicate that measurement of volume weight by either of the methods is satisfactory. Furthermore, they indicate that the volume of the soil in place was measured with an acceptable degree of accuracy in the pit method.

Field capacity. Field capacity values by the two methods should agree (again provided that the volume of the soil in place has been accurately determined). This is actually the case as shown by the data in table 2. The soil employed was that mentioned in connection with table 1. Field capacity by the pit method averaged 0.1 ± 0.88 per cent higher than by the cylinder method. This difference is not significant. In another comparison the field capacity of Berlin clay loam averaged 45.2 ± 1.11 per cent by the pit method and 42.8 ± 1.48 per cent by the cylinder method. The difference of 2.4 per cent is not significant.

TABLE 1

Values for volume weight of Merrimac sandy loam obtained by the cylinder method (schedule A) and by the pit method

STATION	VOLUME WEIGHT BY CYLINDER METHOD (SCHEDULE A)	VOLUME WEIGHT BY THE PIT METHOD	STATION	VOLUME WEIGHT BY CYLINDER METHOD (SCHEDULE A)	VOLUME WEIGHT BY THE PIT METHOD
1	1.033	0.957	7	0.921	0.918
2	0.958	0.875	8	0.885	0.824
3	0.966	0.850	9	0.815	0.992
4	0.769	0.873	10	0.906	0.997
5	1.096	1.018	11	0.878	0.820
6	0.897	0.927	12	0.868	0.886

TABLE 2

Values for field capacity of Merrimac sandy loam obtained by the cylinder method (schedule A) and by the pit method

STATION	FIELD CAPACITY BY CYLINDER METHOD (SCHEDULE A)	FIELD CAPACITY BY PIT METHOD	STATION	FIELD CAPACITY BY CYLINDER METHOD (SCHEDULE A)	FIELD CAPACITY BY PIT METHOD
	<i>per cent volume</i>	<i>per cent volume</i>		<i>per cent volume</i>	<i>per cent volume</i>
1	20.8	24.0	7	22.0	21.4
2	25.6	25.0	8	21.4	26.0
3	20.3	22.2	9	25.1	20.9
4	33.2	28.5	10	20.4	23.3
5	16.9	20.0	11	20.4	17.9
6	25.9	25.6	12	22.0	20.3

Pore volume. Agreement in pore volume values determined by the two methods can be expected only if certain conditions are met. First, the volume of the soil in place must be accurately measured in the pit method. As already indicated, satisfactory accuracy in this respect is evidently attained by use of plaster of paris casts. A second condition necessary for agreement is accuracy in measurement of the volume of the soil material. As indicated in an earlier paper (5) it is known that the procedure in schedule A fails to accomplish complete replacement of air in the soil sample, with the result that the observed volume of the soil material is too large. This causes the pore volume values obtained by the procedure in schedule A to be somewhat lower than true values.

The data in table 3 indicate that pore volume values for Merrimac sandy loam determined by the pit method average 3.3 ± 1.0 per cent higher than values by the cylinder method. This difference is significant. Pore volume of Berlin clay loam by the pit method averaged 66.2 ± 0.40 per cent and by the cylinder method 63.5 ± 0.56 per cent. The difference of 2.7 per cent is significant.

Air capacity. In both methods air capacity values are based on the difference between pore volume and field capacity. Consequently, errors in either will result in errors in air capacity. It has been shown that values for field capacity by the two methods are not significantly different, but the cylinder method

TABLE 3

Values for pore volume of Merrimac sandy loam obtained by the cylinder method (schedule A) and by the pit method

STATION	PORE VOLUME BY CYLINDER METHOD (SCHEDULE A)	PORE VOLUME BY PIT METHOD	STATION	PORE VOLUME BY CYLINDER METHOD (SCHEDULE A)	PORE VOLUME BY PIT METHOD
	<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
1	56.4	61.6	7	61.4	66.8
2	60.2	65.4	8	60.6	67.5
3	59.5	65.8	9	64.8	60.3
4	66.9	65.5	10	59.4	61.1
5	52.2	60.0	11	62.7	67.0
6	61.4	63.5	12	63.8	64.6

TABLE 4

Values for air capacity of Merrimac sandy loam obtained by the cylinder method (schedule A) and by the pit method

STATION	AIR CAPACITY BY CYLINDER METHOD (SCHEDULE A)	AIR CAPACITY BY PIT METHOD	STATION	AIR CAPACITY BY CYLINDER METHOD (SCHEDULE A)	AIR CAPACITY BY PIT METHOD
	<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
1	35.6	37.6	7	39.4	35.3
2	34.6	40.4	8	39.2	41.5
3	39.2	43.6	9	39.7	39.4
4	33.7	37.0	10	39.0	37.8
5	35.3	40.0	11	42.3	49.1
6	35.5	37.9	12	41.8	44.3

(schedule A) leads to low values for pore volume. In view of this, one would expect air capacity values by the cylinder method to be too low. This is confirmed by the data in table 4. Analysis of these data indicates that air capacity by the pit method averages 2.4 ± 0.89 per cent higher than by the cylinder method. This difference is significant. Air capacity of Berlin clay loam by the pit method averaged 0.7 per cent higher than by the cylinder method, but this difference is not significant.

Specific gravity. Specific gravity by both methods should agree if the absolute volume of the soil material is accurately determined. As pointed out in the

discussion of pore volume, however, the cylinder method results in values that are too high. This in turn causes the specific gravity values to be too low. Values in table 5 bear out this view. Specific gravity determined by the pit method averaged 0.20 ± 0.04 higher than by the cylinder method. This difference is significant. In Berlin clay loam, specific gravity by the pit method averaged 0.14 higher than by the cylinder method. The difference is significant.

TABLE 5

Values for specific gravity of Merrimac sandy loam obtained by the cylinder method (schedule A) and by the pit method

STATION	SPECIFIC GRAVITY BY CYLINDER METHOD (SCHEDULE A)	SPECIFIC GRAVITY BY PIT METHOD	STATION	SPECIFIC GRAVITY BY CYLINDER METHOD (SCHEDULE A)	SPECIFIC GRAVITY BY PIT METHOD
1	2.37	2.49	7	2.39	2.76
2	2.41	2.53	8	2.25	2.54
3	2.38	2.48	9	2.32	2.50
4	2.32	2.53	10	2.23	2.56
5	2.29	2.54	11	2.35	2.48
6	2.32	2.54	12	2.40	2.50

TABLE 6

Values for pore volume of Merrimac sand obtained by the cylinder method (schedule B) and by the pit method

STATION	PORE VOLUME BY CYLINDER METHOD (SCHEDULE B)	PORE VOLUME BY PIT METHOD	STATION	PORE VOLUME BY CYLINDER METHOD (SCHEDULE B)	PORE VOLUME BY PIT METHOD
	<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
3A	47.6	46.5	1AN	59.5	59.9
4A	47.3	49.7	2AN	61.0	60.4
5A	45.6	46.3	3AN	57.0	60.5
7A	46.9	49.4	4AN	56.9	56.7
10A	46.6	46.4			

Cylinder method (schedule B) vs. pit method

The treatment used to remove air from the samples was the same in both of these methods, namely, evacuation at room temperature for 2 to 3 hours with occasional shaking. The vacuum used was equal to 15 inches of mercury.

Volume weight and field capacity values by the cylinder method are the same in schedules A and B.

Pore volume. A comparison of the values in table 6 shows that in Merrimac sand, pore volume by the pit method averages 0.8 ± 0.53 per cent higher than by the cylinder method. This difference is not significant. In Berlin clay loam, pore volume by the pit method averaged 66.2 ± 0.40 per cent and by the cylinder method 66.8 ± 0.48 per cent. The difference of 0.6 per cent is not significant.

Air capacity. With similar values for field capacity and pore volume by the two methods, it follows that values for air capacity will also be similar. In neither Merrimac sand nor Berlin clay loam were air capacity values by the pit method significantly different from those obtained by the cylinder method.

Specific gravity. Analysis of the data in table 7 shows that specific gravity values by the cylinder method average 0.02 ± 0.01 higher than by the pit method. This difference is not significant. The specific gravity of Berlin clay loam averaged 2.57 ± 0.01 by the cylinder method and 2.50 ± 0.02 by the pit method. In this case the difference of 0.07 is significant. No explanation for this difference is apparent.

TABLE 7

Values for specific gravity of Merrimac sand obtained by the cylinder method (schedule B) and by the pit method

STATION	SPECIFIC GRAVITY BY CYLINDER METHOD (SCHEDULE B)	SPECIFIC GRAVITY BY PIT METHOD	STATION	SPECIFIC GRAVITY BY CYLINDER METHOD (SCHEDULE B)	SPECIFIC GRAVITY BY PIT METHOD
3A	2.61	2.61	1AN	2.51	2.49
4A	2.61	2.59	2AN	2.55	2.50
5A	2.58	2.62	3AN	2.55	2.51
7A	2.64	2.63	4AN	2.62	2.54
10A	2.61	2.62			

SUMMARY

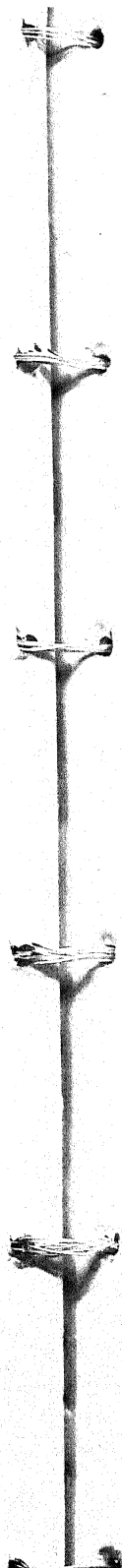
The data presented indicate that volume weight, pore volume, field capacity, air capacity, and specific gravity can be measured by the pit method, employing loose samples of soil, with essentially the same results as are obtained by the cylinder method (schedule B), employing samples of soil in place. Consequently, the pit method provides a means for investigating these physical properties in soils which, because of the presence of rocks, cannot be sampled by cylinders. For work in soils relatively free from rocks the cylinder method is more convenient.

Values for pore volume, air capacity, and specific gravity by the pit method differ from values for these properties obtained by the cylinder method (schedule A). The differences noted are essentially the same as those observed when values obtained by the two cylinder method schedules are compared. That is, the cylinder method (schedule A) results in low values for pore volume, air capacity, and specific gravity. This is explained by the fact that the volume of the soil material is less accurately determined in schedule A than in schedule B and the pit method. The two cylinder method schedules and the pit method all lead to the same results for volume weight and field capacity.

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BOOKS

Annual Review of Biochemistry. Edited by JAMES MURRAY LUCK and JAMES H. C. SMITH. Annual Reviews, Inc., Stanford University, California, 1944. Pp. 795. Price, \$5.

The successive volumes of this annual review of the developments in the field of biochemistry are written by specialists in the respective fields covered. One looks forward to each new volume with anticipation of finding something of particular interest to him, and it is always there. For those concerned primarily with soil-plant relationships, this year's volume contains two papers of paramount importance: "The nutritional deficiencies of farm mammals on natural feeds," by C. F. Huffman and C. W. Duncan, and "Mineral nutrition of plants," by F. J. Richards. The other 24 entries cover a wide variety of subjects of more general interest to the readers of this Journal. They deal with oxidations and reductions, enzymes, the chemistry of carbohydrates, lipids, proteins, amino acids, phosphorus, and hormones; the metabolism of phosphorus, carbohydrates, fats, proteins, and minerals; the biochemistry of nucleic acids, purines, pyrimidines, malignant tissue, and fungi; and such miscellaneous subjects as steroids, vitamins, alkaloids, synthetic drugs, photoperiodism, chloroplast pigments, growth-regulating substances, and histochemistry. The publications of some 4500 authors are covered by the current volume. Every person interested in the nutrition of plants and animals and in the chemistry of the compounds they contain will need this volume for ready reference.

A Laboratory Manual of Physiological Chemistry. Fifth edition. By D. WRIGHT WILSON. The Williams & Wilkins Company, Baltimore, 1944. Pp. 269. Price, \$2.50.

This manual is divided into two parts, the first dealing with inorganic constituents, standard acid and alkali, electrolytic dissociation, colloids, alcohols, aldehydes, esters, proteins, and fats, and the second with saliva, gastric juice, pancreatic juice, milk, blood, bone, muscle, cell nucleus, bile, urine, and dietary deficiencies. Tables of logarithms and atomic weights are appended. Half of the pages are blank for note-recording purposes. The manual is intended for teaching rather than for reference purposes, but some references are given. Although designed primarily for use in animal physiology, many of the methods would be found useful in plant physiology and chemistry as well.

Practical Farming for the South. By BENJAMIN F. BULLOCK. The University of North Carolina Press, Chapel Hill, 1944. Pp. 510, figs. 199. Price, \$2.50.

Written primarily for those south of Mason and Dixon's line, this book is nevertheless equally if not more interesting to those living farther north. The fundamentals of farming are much the same, no matter in which area one lives, but the agriculture of the South is built around a very different climate and set of crops. The book is divided into three parts: plant production, animal

production, and farm financing and literature. Its primary purpose is to give specific instructions on what to do and how to do it, and the illustrations are nicely designed to amplify the instructions. From reading the book, one gets the impression that the author has his feet firmly planted in the soil and that he is intrigued by the opportunities not only for making a living but for living well in the South.

Practical Methods in Biochemistry. Fourth edition, revised. By FREDERICK C. KOCH and MARTIN E. HANKE. The Williams & Wilkins Company, Baltimore, 1943. Pp. 353, figs. 20. Price, \$2.25.

This book assumes an understanding of general chemistry, physics, and biology. It deals with the chemistry of cell constituents, the chemistry of the digestive tract, and the chemistry of blood and urine. The last two chapters are concerned with colorimetric methods for vitamins and chemical tests for hormones. The appendix comprises 61 pages and contains a variety of useful information on laboratory procedures, colorimeters, and standard solutions and reagents. Students of any phase of biochemistry, whether plant or animal, will find this volume of interest and value.

THE EDITORS.

PERMEABILITY MEASUREMENTS ON DISTURBED SOIL SAMPLES¹

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Few workers have investigated the extent to which laboratory permeability measurements on disturbed samples of arable soils are indicative of field percolation rates. In many cases permeability values obtained in the laboratory may not even approximate the field percolation rates. Nevertheless, much time and expense can be saved, especially in dealing with saline and alkali soils, by preliminary laboratory studies on the response of these soils to soil amendments and to waters of different chemical composition and concentration. Preliminary tests indicate that, regardless of the correlation between laboratory and field percolation rates, the *relative* change in permeability obtained in the laboratory as a result of any given treatment is closely correlated with the *relative* change in percolation rate obtained in the field as a result of a similar treatment. Furthermore, recent work by the author and others indicates that, because of its extreme sensitivity, soil permeability as determined in the laboratory may be one of the best, if not the best, criterion of soil structure available. It was deemed advisable, therefore, to examine carefully the factors operative in the laboratory measurement in order to select an easily reproducible yet simple procedure, suitable for running large numbers of samples simultaneously. Some of the results obtained, which may be of use to workers interested in the permeability of arable soils, are presented together with a brief discussion of some important factors involved in soil permeability determinations. No attempt has been made to present a complete or critical review of the subject. Tables of numerical values have been omitted for the sake of brevity.

APPLICATION OF DARCY'S LAW TO SOIL PERMEABILITY MEASUREMENTS

The movement of fluids through capillary tubes was first studied by Hagen (11) and by Poiseuille (15). They found that the rate of flow is proportional to the hydraulic gradient. Darcy (6), on the basis of investigations on the flow of water through filter-sands, verified this observation and suggested its application to problems of water movement through water-bearing materials. Darcy's conclusion, now known as Darcy's law, can be expressed in a very general formula:

$$v = P \phi \quad (1)$$

in which v is the velocity of moving water; P is referred to variously as the permeability (the use in this paper), the Darcy coefficient of permeability, the co-

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efficient of permeability, or the transmission constant; and ϕ is the potential gradient (change in static hydraulic head per unit distance along the average flow line).

The permeability of a porous material may be defined, therefore, as the volume of fluid flowing through unit cross-sectional area per unit of time per unit potential gradient. For purposes of calculation the following formula is ordinarily used:

$$P = \frac{Ql}{TAh} \quad (2)$$

in which P is the permeability, Q the volume of water, T the time, A the cross-sectional area, l the length under consideration, and h the loss in hydraulic head through length l . P has the dimensions of velocity (LT^{-1}) if l and h are expressed in the same unit.

Permeability, in order to be a function only of the water-bearing material, should be defined also in terms of the acceleration due to gravity, g , and the density, d , of water. Changes in permeability caused by changes in g and d are extremely small, however, and it is not ordinarily necessary to correct for them, especially in dealing with soils. A correction for temperature, t , is often used in equation (2); this will be discussed more fully later.

The following extremely useful equation³ is derived from equation (2):

$$P = \frac{L}{\frac{l_1}{p_1} + \frac{l_2}{p_2} + \dots + \frac{l_n}{p_n}} \quad (3)$$

where P is the average over-all permeability of a column of porous material of length L , and p is the permeability and l the length of each of the components of the column. By means of equation (3) the effect of stratification on permeability can be accurately evaluated by solving for over-all column permeability, having the permeabilities and the lengths of the components of the column.

Invariably, there is some loss in hydraulic head due to the passage of water through the soil-retaining screens (sand, filter paper, wire gauze, ceramic discs, etc.) which are used to hold the soil in the permeameter. It is usually desirable to evaluate this loss in order to arrive at the true permeability value for the soil. This can be done in two ways: first, the permeabilities of soil plus retaining screen and of retaining screen alone can be determined separately, and the values obtained substituted in equation (3); and second, the permeability can be calculated from the flow rate per unit area and pressure readings taken with manometer tubes inserted into the soil sample through the walls of the container. The insertion of several manometers makes this method especially valuable for studying (a) homogeneity of packing (or of structure in the case of cores), (b)

³ This equation was derived by J. E. Christiansen and the author in 1943. A similar equation was given later by Terzaghi (21).

development and location of zones of maximum and minimum permeability, (c) effects of soil-retaining screens, (d) surface sealing and outlet effects, (e) the localized and general effects on permeability of fertilizer or salt applications, and (f) elimination of air.

There has been some difference of opinion as to whether Darcy's law applies to the movement of water through porous materials at all hydraulic gradients, particularly at very high and very low gradients. It was first shown by Reynolds (16), and subsequently by others, that velocity varies directly as the loss in hydraulic head as long as flow is laminar (streamlined), and also that laminar flow changes to turbulent flow at much higher velocities than are ordinarily encountered in soils. With regard to low gradients, recent tests (22) "show rather conclusively that . . . the rate of flow varies directly as the hydraulic gradient, down to a gradient of 2 or 3 inches to the mile, and that there are indications that Darcy's law holds for indefinitely low gradients."

Darcy's law applies to the movement of moisture through *both* saturated and unsaturated materials. Determination of the hydraulic gradient through unsaturated materials is extremely difficult, however, and has been attempted in a few cases only (14, 17).

A vast amount of research has been done on the horizontal movement of ground water. Hydrologists have developed methods for determining the hydraulic gradient, but the flow rate and the cross-sectional area of the water-bearing materials have been difficult to ascertain. Much work has been done on infiltration into undisturbed soil; in these studies, for the most part, no attempt was made to determine the hydraulic gradient, hence soil permeability could not be calculated.

The percolation of water through soil samples artificially packed in the laboratory has been studied by many investigators. King (13), Slichter (19), Greene and Ampt (9), and others have attempted to formulate general equations for the determination of permeability based upon sand grain size, type and arrangement of particles, effective specific surface, soil porosity, etc., but these equations have been useful only in special cases. Several workers (1, 7, 20) have shown that certain pore-size distribution measurements correlate well with short-time percolation tests. Pore-size distribution measurements, however, are no more easily made than are direct permeability measurements, and application of the results to practical agricultural problems is more difficult, especially in dealing with highly dispersed or water-unstable soils. Harris (12), Bodman (2, 3), and others have indicated the effects of some salt solutions, time, texture, volume weight, etc., upon the rate of movement of water through soils. Slater and Byers (18), among others, have obtained good agreement in most cases between natural cores and artificially packed tubes of the same soil.

METHODS FOR DETERMINING PERMEABILITY IN THE LABORATORY

Indirect

Permeability is determined indirectly by analyses of the size, shape, and arrangement of the soil particles, or by some related property such as "pore-size

distribution" or "noncapillary porosity." These methods have not been of particular value except in special cases such as evaluation of probable permeability to air. They are not, as yet, sufficiently accurate for general use, nor do they usually involve a saving in effort or expense. Engineers have found the Terzaghi consolidation test of considerable value in calculating the permeability of foundation materials. The method is not applicable, however, to arable soils.

Direct

Permeability (P) is calculated directly from the rate of movement of water through soils according to equation (2) when the hydraulic head is kept constant, and according to the following integrated form of equation (2) when the hydraulic head is allowed to vary:

$$P = \frac{al}{AT} \log_e \frac{h_1}{h_2} \quad (4)$$

in which a is the cross-sectional area of the water reservoir; l , A , and T are the same as in equation (2); and h_1 and h_2 are the hydraulic heads at the start and end of the time interval T , respectively.

The variable-head permeameter was developed for use with materials of very low permeability and has definite advantages over the constant-head methods for these materials. These advantages are ease of control of head, and insignificance of effect of evaporation on results. This method has several disadvantages, however, which make its use inadvisable for permeability measurements on most arable soils. These disadvantages are: amount of equipment necessary to run large numbers of samples simultaneously; possible effect on the soil of periodical refilling of the reservoir; and effect of air entrapped in the soil on the calculated permeability. This last point is discussed fully in another paper from this laboratory (5).

In the constant-head permeameter the water level in the supply reservoir remains constant and the water that passes through the soil is measured or weighed. This method has the following advantages: the soil is not disturbed during the entire run; the effluent is quickly and accurately measured; the reservoir requires a minimum of attention; and, most important, easily available and inexpensive equipment can be utilized. This method has at least two disadvantages: maintenance of a constant head is often troublesome; and a constant head is seldom encountered under natural conditions.

THE SOIL PERMEAMETER

Shape, length, and diameter

The soil-containing section of the permeameter should be cylindrical and of uniform cross-sectional area to prevent restriction of flow. No significant difference in soil permeability was found upon varying the permeameter length from 1 to 34 inches, or the diameter from 1 to 6 inches. Nonuniformities in packing and particle size distribution are diminished, however, by increases in permeameter diameter and length.

Water outlet

For the reasons given below, water is passed downward through the soil samples. A "drip-point" water outlet is not so satisfactory as an overflow outlet principally because of the difficulty in ascertaining the exact point of zero hydraulic head. For convenience, the drip-point outlet is used when small differences in permeability are not important.

Soil-retaining screen

The soil must be held on a screen which is much more permeable than the material to be tested and it must be held in such a manner that water movement is relatively unimpeded and soil sloughing is prevented. Sand, cotton, glass wool, filter paper, perforated metal disks, wire gauze, asbestos, and thin fiber-glass screens have been used for this purpose. Used singly, none was found to be entirely satisfactory. Perforated brass disks covered with a thin layer of coarse asbestos, sand supported by a thin fiber-glass screen, and lathing screen covered by one thickness of "fast" filter paper have been quite satisfactory. The first two are preferable for indefinitely long tests; the third is preferable for short tests because of uniformity and ease of preparation.

Head controls

Here are three principal types of constant water-level controls: overflow system, Mariotte or inverted flask, and float valves. The overflow system requires a minimum of equipment and attention, but it also requires a large, easily available water supply. The Mariotte flask does not require excess water, but unintentional disturbance of the soil is almost unavoidable, and difficulties are encountered in recharging the reservoir. An inexpensive and highly accurate float valve devised by the author (see figure 1) has proved very satisfactory for head control, especially when large numbers of samples are run simultaneously. The fluctuation of the water level is automatically controlled within less than 0.5 mm., and the head can be adjusted to any height. The float valve consists of an electric light bulb firmly attached to a valve core screwed down into an automobile or bicycle inner-tube valve stem. (The valve core must have most of its coiled spring removed.) The valve stem is held firmly upright in a small delivery reservoir by means of a one-holed rubber stopper set in an opening in the bottom of the reservoir. The lower end of the valve stem is connected to a large water reservoir by a convenient siphon arrangement. The water level in the small reservoir can be adjusted by slipping the valve stem up or down in the rubber stopper; water is delivered through one or more side arms located below the water line. In this manner one float valve has served as many as 24 soil permeameters simultaneously; for convenience, the permeameters are usually connected in series.

Hydraulic gradient

According to Darcy's law, permeability is independent of the hydraulic gradient. Tests by the author in which the gradient was varied from 0.1 to about

20 failed to disclose any significant variation in permeability. Christiansen's work (5) indicates that as long as entrapped air is present, changes in gradient bring about variations in pressure within the soil column and so affect soil permeability calculations slightly.

FLUIDS USED IN PERMEABILITY MEASUREMENTS

The permeability of a porous medium is, presumably, a constant determined only by its structure and independent of the nature of the fluid passing through it. For this reason gases, nonpolar liquids, and water have been used, and several

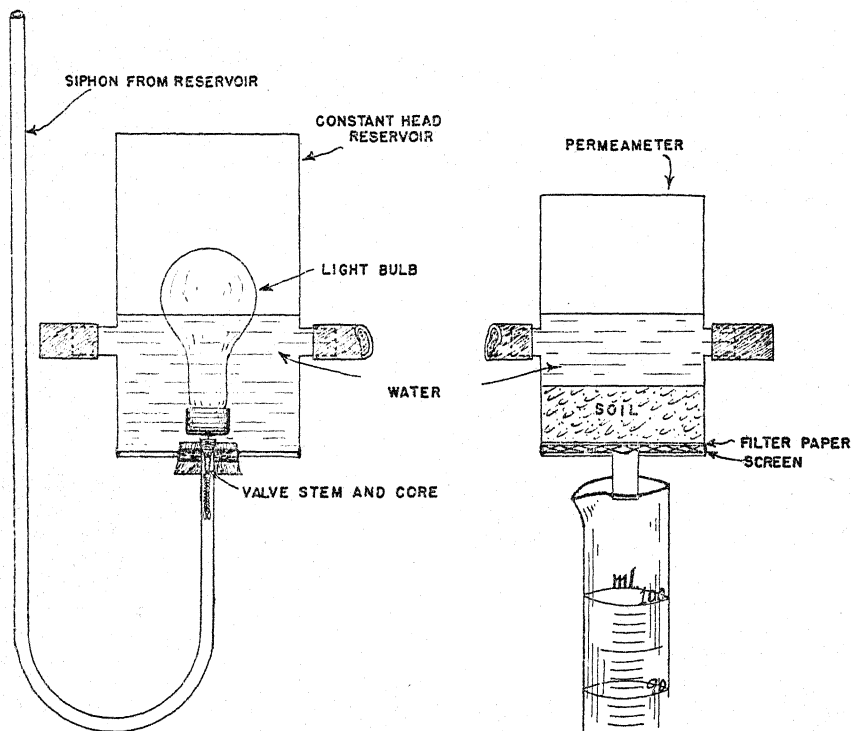


FIG. 1. CONSTANT HEAD RESERVOIR AND SOIL PERMEAMETER

investigators (9, 13) have shown that for certain media the same permeability value is obtained regardless of the fluid employed. It has been demonstrated by Greene and Ampt (9) and others, however, that the presence of hydrophilic colloids precludes the use of anything but water in measuring the permeability of soils to water.

EFFECT OF VISCOSITY AND TEMPERATURE

Since water is almost always the fluid of interest in soil permeability, its viscosity, except for variations due to temperature and electrolyte content, usually contained in the coefficient of permeability. Variations in viscosity due

to dissolved solids can ordinarily be neglected, since increasing the electrolyte content of water from 0 to 5,000 p.p.m. results in an increase in viscosity of less than 1 per cent. The viscosity of water decreases approximately $2\frac{1}{2}$ per cent per degree Centigrade rise in temperature. Hydrologists have long corrected permeability values to standard temperatures, and have been justified in so doing when dealing with noncolloidal materials. Work by Griffiths (10) and unpublished data by the author and others, however, indicate that in soils a given change in temperature usually does not result in an equivalent change in flow rate. That is, the relationship between flow of water through soils and viscosity is not a direct one, presumably because of soil-water reactions which are affected by temperature changes. Reference of permeability values to a standard temperature should not be made, therefore, in dealing with soils; however, application of viscosity corrections when the temperature fluctuates widely usually results in more uniform permeability values. Viscosity corrections were applied in these studies only when the temperature fluctuation during a given test exceeded 2°C.

DIRECTION OF FLOW AND ENTRAPPED AIR

Most investigators are of the opinion that the water must flow upward in order to avoid the entrapment of air in the soil pores, and their permeameters are designed accordingly. Retention of a soil sample in an upward-flow permeameter is difficult and complicated, however, especially when high hydraulic gradients are employed, since the sample must be confined, usually by a spring arrangement, to prevent it from "floating." This requires relatively complicated and expensive equipment and procedures not ordinarily available. The relative merits of upward and downward flow were, therefore, carefully investigated. Briefly, it was found that no more air was trapped in the soil pores by downward flow than by upward flow, and the permeability values obtained by the use of both types of flow were different in the early stages of flow, but later were in excellent agreement (see figure 4). As a result, downward flow is employed almost exclusively at this laboratory, and with excellent results. Christiansen (5) has reported in detail on the effects of entrapped air on soil permeability measurements.

TEXTURE, VOLUME WEIGHT, AND WATER CONTENT DURING PACKING

The exact relationship between soil permeability and porosity or the factors which affect porosity may not be clarified for some time. In general, permeability decreases with increases in clay or silt content. The relationship between soil permeability and porosity is complicated, however, by differences in the dispersion of the fine soil particles, and by the properties of the suspended clay particles, which are affected by the electrolyte content of the water surrounding them, the nature of their replaceable cations, and their mineralogical composition. Bodman (2) has shown that the initial volume-weight increases are extremely important and that textural differences have very little significance at very high volume weights for soils finer than fine sandy loams. As Cary *et al.* (4) have

pointed out: "that the wide range or narrow range of void sizes may be imparted to the soil at will, with absolutely no variation in density being necessary, is proved by the extreme range in permeability among groups of samples compacted at very nearly identical densities but at different moisture contents."

It is evident that the method of packing and the moisture content of the soil when packed must be selected arbitrarily. For convenience and reproducibility, soils should be screened and packed air-dry as indicated elsewhere in this paper.

EFFECT OF SIEVE SIZE ON PERMEABILITY

In the preparation of soils for laboratory examination, air-drying and sieving are usually necessary, and the 2-mm. sieve is most often used. Permeability measurements indicated, however, that the 2-mm. sieve might not be satisfactory for all soils. The stability of soil aggregates in water, a property dependent to a considerable degree upon mineralogical composition, is intimately related to soil permeability. Therefore, samples of two soil series which differ widely in mineralogical composition and water stability, the Yolo and the Aiken, were selected for this investigation. These soils by no means represent the extremes which might have been selected, the Yolo, however, is far more representative of western irrigated soils than is the Aiken. The Yolo, a fine sandy loam, contains a clay predominantly montmorillonitic in composition and is already relatively highly dispersed or is very easily dispersed in water. The Aiken, a clay loam, is high in kaolinite and is well aggregated and very difficult to disperse in water. Samples of each of these soils were gently crushed to pass through 2-mm., 1-mm., 0.42-mm., 0.15-mm., and 0.075-mm. sieves, and permeability measurements were made on each sample. The results are presented graphically in figure 2.

Examination of figure 2 discloses that the well-aggregated Aiken soil acts like sand, in that the permeability decreases with decreases in the diameter of the sieve openings through which the soil has been passed. Undoubtedly, other physical measurements on soils of this type are affected similarly by sieve size. Choice of a sieve size for well-aggregated or water-stable soils is, therefore, entirely arbitrary and must depend upon the proposed use of the information.

The permeability of a dispersed or easily dispersed soil (e.g., the montmorillonitic Yolo) should be, for the most part, independent of sieve size. It is evident from figure 2 that though sieve size may be a factor in brief permeability tests, it is not an important factor in long-continued tests on soils like the Yolo. As a matter of routine, therefore, the 2-mm. sieve is used for long-time tests on easily dispersed soils, and the 1-mm. sieve is used for all short-time tests and for long-time tests on well-aggregated soils.

PACKING TECHNIQUE

Since it is not possible to pack disturbed soil so as to reconstruct its natural arrangement, permeability values obtained in the laboratory upon disturbed soil samples frequently may be poorly correlated with field percolation rates. Hence, the author was interested principally in *relative* response to any given treatment, this response being closely related to field behavior. Obviously, therefore,

uniformity of packing within a soil column and between replicate columns was of utmost importance in the laboratory measurements, and so packing was studied in great detail.

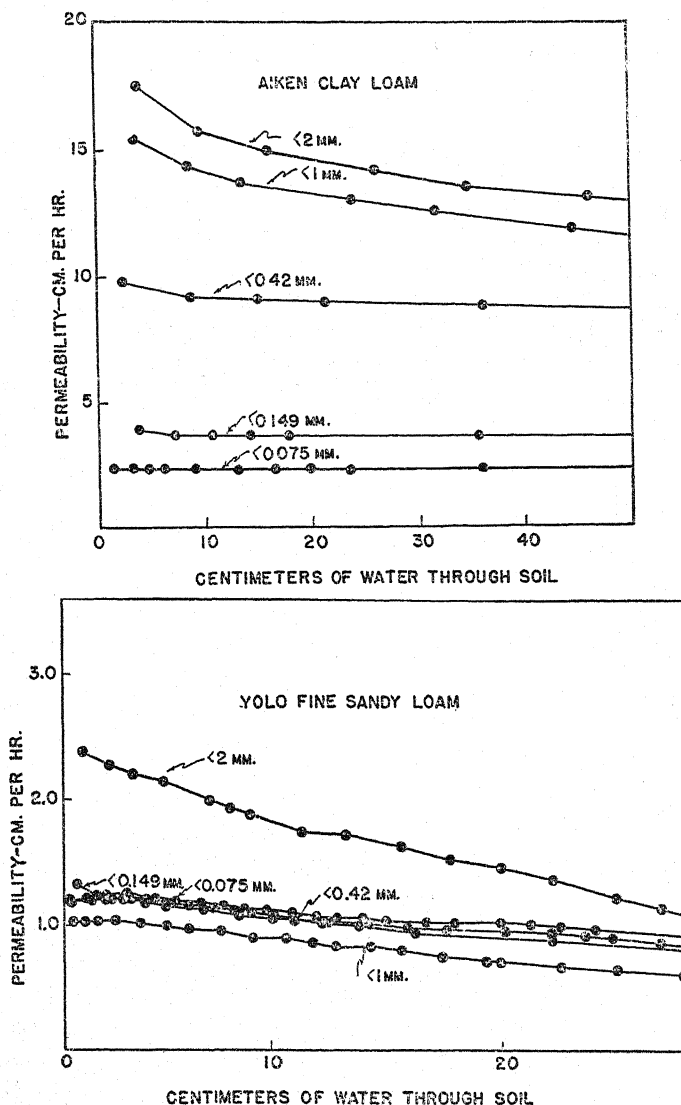


FIG. 2. EFFECT OF SIEVE SIZE USED IN SOIL PREPARATION ON SOIL PERMEABILITY

Soils were packed oven-dry; air-dry; and with varying percentages of moisture by a propeller type of filler and impactor, by a variable speed vibrator, by tamping from above, and by dropping the soil-filled permeameter upon a solid wooden block ("impact" method). As has been indicated, the soil must be packed dry in order to give reproducible permeability values, and oven-drying

has no advantage over complete air-drying. The vibrator was not able to impart to the loose soil a volume weight as high as that found in the field, and the correlation between volume weight and permeability on samples packed by vibration was not good. The propeller and impactor and the tamping method gave layers of varying permeability as indicated by calculations from manometer readings. Dropping the soil-filled permeameter squarely upon a solid wooden block an adequate number of times was found to be most satisfactory as regards uniformity of packing, control of volume weight, and reproducibility of permeability values.

The effect of number of impacts (number of times the soil-filled permeameter was dropped upon the wooden block) upon soil permeability, in the absence of high bearing pressures such as are encountered in engineering work, was studied next. The results on two soils are presented graphically in figure 3. The well-aggregated kaolinitic Aiken soil again acts much like a sand, in that a relatively few impacts are sufficient to reduce the permeability (and the volume weight) almost to a minimum. Soils like the Aiken evidently require a certain amount of compaction, beyond which the permeability values are but slightly affected. The montmorillonitic Yolo soil, however, responds continually to impaction, and the permeability (and to a lesser extent the volume weight) is dependent upon the number of impacts received. Selection of the number of impacts to be given soils of this type is, therefore, entirely arbitrary. Some workers pack to original field density, and this may have some merit. Figure 3 indicates that extreme caution is necessary in interpreting permeability data obtained on disturbed samples of soils like the Yolo unless sound procedures are adhered to rigidly. In highly precise studies, the packing characteristics of each soil must be known.

In these studies short columns ($1\frac{1}{2}$ to 4 inches long) of all soils were arbitrarily given about 20 impacts from a height of 1 inch, the exact number varying somewhat with column length.

WETTING TECHNIQUE

Initially, upward flow was used in determining soil permeability. It was soon found more expedient to have downward flow, but the soils still were wetted carefully from below for the purpose of displacing as much air as possible from the soil pores. Other experiments showed that upward water movement displaced little, if any, more air from the soil pores than did downward water movement. Thereupon, the effect of initial wetting upon soil permeability was studied. Some of the results obtained are presented in figure 4. It is evident that the manner of wetting is not important in long-continued permeability tests on these soils but that it is of considerable influence in short tests. The reason for this is not apparent. It may be due to differences in the local movement of soil particles and in the manner in which air is trapped by the two different flow directions.

It is of interest to note that the water-stable Aiken soil is but slightly affected by 24 hours of slaking, whereas the Yolo is markedly affected. This definitely indicates that the difference in the permeability curves is not due to trapped air

since both (A) and (B), in figure 4, were slowly wetted from below and presumably should have equal permeabilities. Furthermore, though displacing the air from below usually results in high initial permeability values (fig. 4), at least two soils have been tested in which the reverse is true. As has been em-

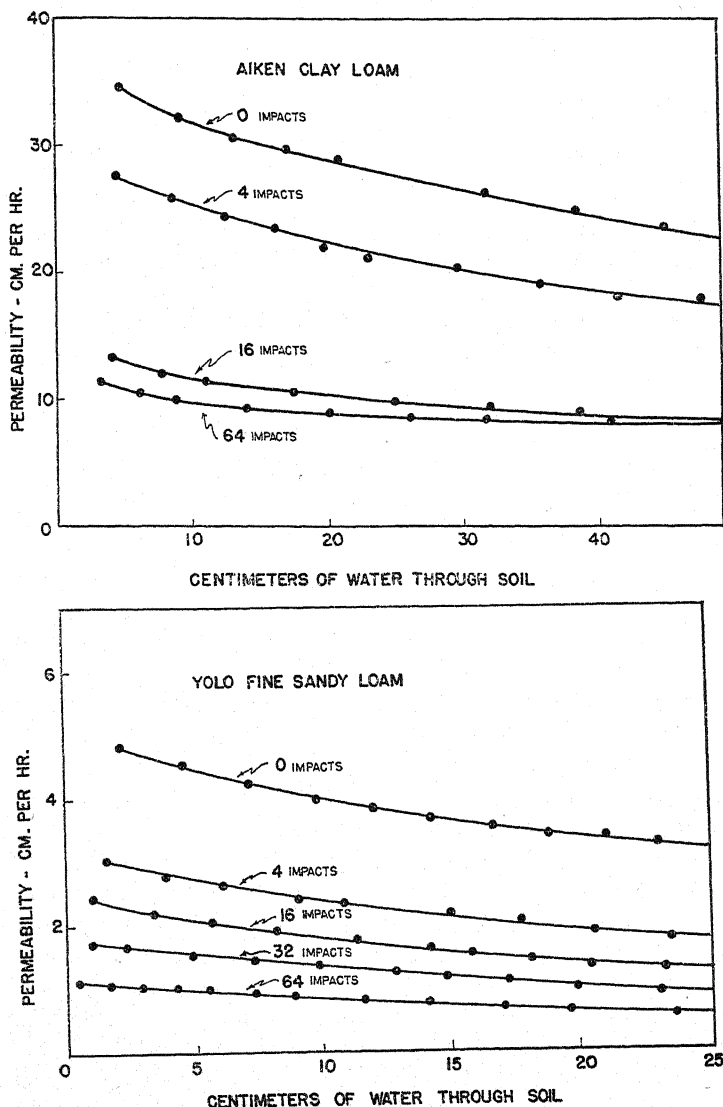


FIG. 3. EFFECT OF NUMBER OF IMPACTS UPON SOIL PERMEABILITY

phasized, however, the relative changes in permeability, and not the absolute values, are of paramount importance. Any convenient procedure may be adopted, therefore, provided it does not seriously alter the shape of the flow curves. Application of water to the dry soil from above is convenient, is similar

to field application, and gives results in excellent agreement with other methods of wetting, especially if the tests are long-continued.

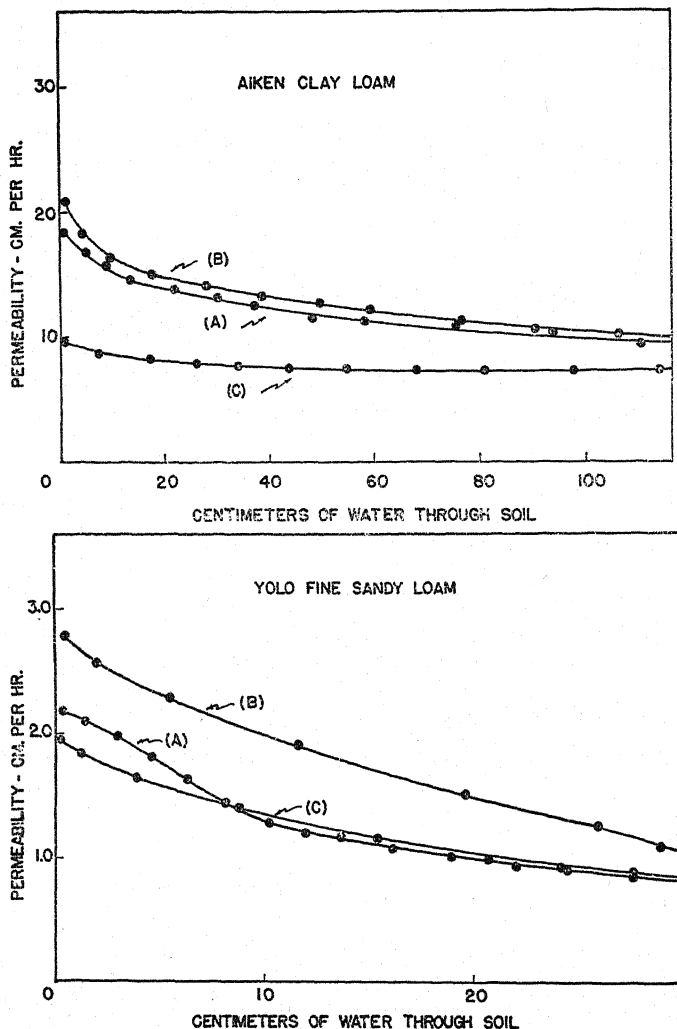


FIG. 4. EFFECT OF INITIAL WETTING ON SOIL PERMEABILITY

Downward flow after: A, wetting from below and soaking 24 hours; B, barely wetting from below; and, C, no preliminary wetting.

VARIABILITY OF THE PERMEABILITY "CONSTANT" WITH TIME

During the course of these experiments it was found that permeability decreased markedly with continued downward flow (fig. 4). Similar observations were made previously by a number of workers (3, 8). Bodman (3), who has made the most comprehensive study of the effect of long-continued percolation, says: "Explanation of the great decreases in saturated water-permeability of all

of the soils examined seems to lie in the early removal of electrolytes and subsequent gradual dispersion and rearrangement of the clay particles so that the conducting pores are reduced in size more or less permanently." Additional experimentation by the author and by J. E. Christiansen, of this laboratory, substantiates Bodman's findings and also indicates that microbiological growth within the soil column may prove to be of considerable importance, especially in long-time permeability tests.

ELECTROLYTE CONCENTRATION

A correct evaluation of the influence of electrolyte concentration upon soil permeability is difficult because of many complicating factors such as soil texture, degree of dispersion, mineralogical composition, and base-exchange status. The last-named variable, especially, leads to difficulty, since base status is a function of the concentration as well as the composition of the solution bathing the soil. Most workers have long recognized these facts, and realize, furthermore, that no permeability determination that ignores the effect of dissolved salts is entirely applicable to a practical problem. Because of the apparent complexity and hitherto limited use of permeability determinations, however, little pertinent information has been collected on the effect of electrolyte concentration on permeability measurements. This subject is now being investigated further by the author.

In general, because of its effect on soil dispersion, the lower the salt concentration, the lower the soil permeability. In preliminary tests it was found that decreasing the electrolyte content of the percolating water from 10,000 to 40 p.p.m. (3 gram-equivalent weights of CaCl_2 to 2 of NaCl) decreased the permeability of Aiken clay loam from 10.2 to 7.3 cm. per hour, and of Yolo fine sandy loam from 2.8 to 0.3 cm. per hour (comparisons were made when 12 inches of solution had passed through each soil sample). Some other soils showed very much greater response to changes in electrolyte concentration. Pending further information, for ordinary permeability measurements it seems best to use the water used in regular irrigation practice upon the soil in question. For specific problems other waters may be more suitable.

CHEMICAL COMPOSITION OF WATER

A factor which has received much attention in soil reclamation, but which is often overlooked in permeability studies, is the chemical composition of the water used for the permeability test. Some alkali soils tested at this laboratory are hundreds of times more permeable to tap water (280 p.p.m. of mixed salts, approximately 40 per cent of which are sodium salts) than they are to distilled water or to low-salt waters containing a high percentage of sodium. Calcium is the principal absorbed cation of the colloidal complex of most agricultural soils. In general, these soils are reasonably permeable to water and have a favorable physical condition for cultivation and crop production. When water containing a high percentage of sodium salts comes in contact with or is percolated through these soils, base exchange takes place and sodium ions replace a considerable por-

tion of the absorbed calcium ions. Some soils remain moderately permeable when leached with high-sodium water as long as the salt content remains fairly high because the presence of the salt tends to keep the soil flocculated. If the high-sodium water is replaced by a water of considerably lower salt concentration, the soil will disperse immediately and become sticky and relatively impermeable, regardless of the chemical composition of the latter water.

Characteristic curves⁴ for an agricultural soil are shown in figure 5 (note that the ordinate of the graph is plotted to a logarithmic scale). The curves show the changes in permeability that occurred with the amount of water which passed through the soil. This soil is typical of many others tested, in that

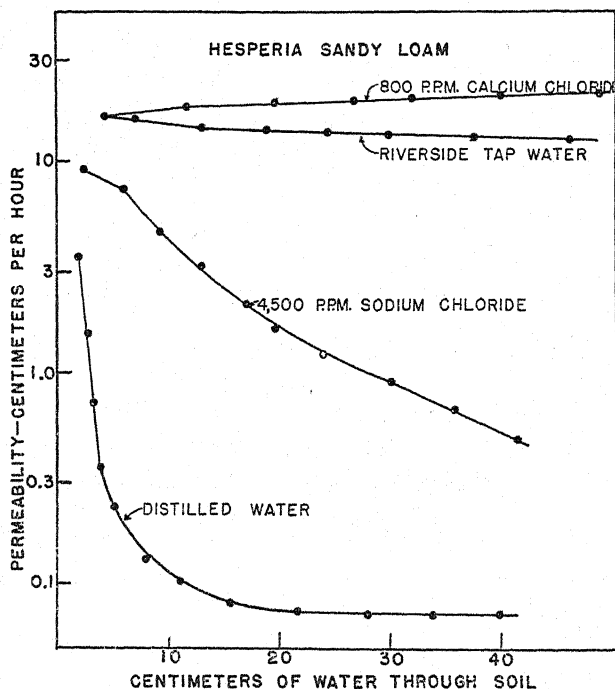


FIG. 5. PERMEABILITY OF AN AGRICULTURAL SOIL AS INFLUENCED BY WATER COMPOSITION

it shows marked differences in permeability to distilled water as compared with the aforementioned tap water or with waters containing only a few hundred parts per million of various calcium salts. It will be noted that the Hesperia soil is more permeable to a 4,500 p.p.m. sodium chloride solution than it is to distilled water. On subsequent leaching with distilled water, however, the soil became virtually impermeable. One soil tested was 20 times as permeable to tap water and 35,000 times as permeable to a water containing 800 p.p.m. of calcium chloride as to distilled water.

These and other data indicate that the chemical composition of the percolating

⁴ These curves were published by J. E. Christiansen and the author in a discussion of reference (4).

water and the chemical changes brought about by it may be of the utmost importance in permeability tests on colloid-containing materials.

REPLICATION

From the foregoing discussion it is evident that, although permeability values are easily obtained in the laboratory, highly standardized arbitrary techniques are required if valid comparisons are to be made between soils and between treatments. These techniques are easily acquired, however, and very satisfactory results may be obtained with practice. For example, fifteen 200-gm. air-dry samples of each of two soils were packed, as described above, into permeameters. After 2 hours of percolation with Riverside tap water the average permeability of all samples of the first soil was 6.4, the maximum value 7.2, and the minimum value 6.1 cm. per hour; after 24 hours of percolation the average was 5.1, the maximum 5.7, and the minimum 4.8 cm. per hour. For the second soil the average permeability after 2 hours was 0.34, the maximum 0.42, and the minimum 0.31 cm. per hour; after 24 hours of percolation the average was 0.25, the maximum 0.32, and the minimum 0.21 cm. per hour.

As a matter of routine in this laboratory the permeability is usually obtained on triplicate samples. All samples are discarded and the permeability redetermined if the range of values is greater than 50 per cent of the mean permeability value. Pending further research, differences in average permeability of less than 10 per cent are not considered significant.

DISCUSSION

It has been the author's purpose to develop a simple and reliable procedure for making permeability measurements on large numbers of disturbed soil samples simultaneously. The procedure presented herein has widespread applicability, but is particularly suitable for studying the factors which influence water movement in saline and alkali soils. Briefly, it involves air-drying the soil; sieving through 1- or 2-mm. openings; subsampling by means of a small ore sampler; weighing; transferring to a permeameter; leveling with a spatula; packing by dropping the permeameter solidly about 20 times on a wooden block provided with a hole to accommodate the water outlet of the permeameter; connecting the permeameter in series with a constant-head delivery device; introducing water on to the soil, covered initially with filter paper to prevent soil disturbance; collection and measurement of percolate in a graduated cylinder; measurement of hydraulic head and soil column length during water percolation; and calculation of permeability by means of equation (2). One operator can handle 24 to 48 samples simultaneously.

The rate of movement of water through soils is the resultant of a large number of complex factors, both chemical and physical. A few of these factors have been discussed briefly. It is evident that much work must be done before predictions of quantitative significance can be made as to the field response of a soil to a given set of conditions. As previously mentioned, studies on undisturbed soil samples probably are of maximum value, but field cores are obtained and

handled with extreme difficulty, especially in arid regions. Permeability studies on disturbed soil samples have already been and are continuing to be of great value in extending and clarifying quantitative information on specific soil-water-salt interactions. The relatively great response of soil permeability to slight changes in structure makes permeability particularly suitable as a laboratory criterion of soil condition.

The details of the equipment and procedures used in this laboratory are briefly given in this report, since it is felt that an understanding of the factors which influence soil permeability measurements will be of much more value than explicit directions. Comprehension of the more important of these factors should assist in the development of procedures suitable to specific problems.

SUMMARY

Laboratory studies are useful where it is not practical or economically feasible to conduct field trials on soil reclamation and movement of water through soils. Disturbed soil samples can be used advantageously to study the relative changes in percolation rate brought about by specific chemical and physical soil treatments. Some of the factors which influence laboratory permeability measurements are discussed briefly. These are: method of determination; shape and size of permeameter; water outlet; soil retaining screens; water-head controls; hydraulic gradient; fluids; viscosity; temperature; direction of water flow; entrapped air; texture; volume weight, and water content during packing; effect of sieve size; packing technique; wetting technique; variability of permeability with time; electrolyte concentration; composition of water; and replication.

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EFFECT OF ENTRAPPED AIR UPON THE PERMEABILITY OF SOILS¹

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Several investigators (2, 3, 11, 13) have shown that the permeability of a soil, as determined in the laboratory, is not constant but varies considerably with time, when tests are carried on over a period of weeks or months. There are usually three distinct phases during a permeability test: an initial period in which the permeability decreases, in some instances only slightly but in many, to a small fraction of the original rate; a second period during which the permeability increases, in some instances to more than 30 times the previous minimum rate; and a third period when the permeability again decreases gradually but steadily during the remainder of the test. Similar variations have been noted in the rate at which water enters the soil in field plots submerged for long periods.³ The purpose of this paper is to present an explanation, with experimental evidence, for the increase in permeability that occurs during the second phase of the test.

REVIEW OF LITERATURE

Variations in permeability with time were studied by Bodman (2), using distilled water. A sharp decrease in permeability took place during the first few hours of the test. This was followed by a sharp rise, which, for four of the soils, occurred during the first 10 days of the experiment. This in turn, was followed by a rather rapid decrease in permeability for a few days and a more gradual decrease for the remainder of the test. No explanation for the increase in permeability was offered.

Fireman and Bodman (3) plotted the permeability against the volume of percolate to a logarithmic scale, which emphasizes the initial phase of the test, wherein the first decrease in permeability takes place. This decrease was followed by an apparent sudden increase in permeability when the volume of percolate amounted to about 15 times the pore space of the soil.

King (8) found that the flow through certain porous media increased over a period of time without change in pressure. He further found that when the pressure was increased the flow nearly always increased more rapidly than the pressure. The deviations ranged from less than 1 per cent, in some instances to

¹ Contribution from U. S. Regional Salinity Laboratory; Bureau of Plant Industry, Soils, and Agricultural Engineering; Agricultural Research Administration; U. S. Department of Agriculture; Riverside, California; in cooperation with the eleven western states and the Territory of Hawaii.

² Irrigation and drainage engineer. Acknowledgment is gratefully made to Milton Fireman, R. F. Reitemeier, and Betty Mabry for helpful advice and assistance in planning and carrying out these experiments, and to Mrs. Ruth Johnson for much of the routine work and computations involved.

³ Unpublished data of H. L. Haehl (1943) concerning water-spreading experiments.

more than 50 per cent for certain materials. King discussed the possibility of the deviations being due to "entangled" air adhering to the porous material, but ruled out this possibility on the grounds that the increase in flow was too great to have been caused by the rather slight compression of the air. He failed to arrive at a satisfactory explanation for this phenomenon.

Wityn (13) presented a number of permeability-time graphs, but gave no explanation of the increase in permeability that occurred shortly after the beginning of the tests.

The problem of confined air has been discussed by Baver (1), Powers (9), Slater and Byers (11), Free and Palmer (5), Horton (6), and others. They have shown that when soil in a tube closed at the bottom is wetted with water from the top the confined air is compressed. This air confinement causes an appreciable reduction in rate of infiltration as compared with similar experiments where the air is allowed to escape as the water enters the soil. "Confined air" should not be confused with "entrapped air" as discussed in this paper.

Zimmerman (14) has shown that air is entrapped in the pores of soil when the soil is wet by capillarity from below. Smith and Browning (12) have shown that natural soil cores, when wetted under laboratory conditions, are not completely saturated, but contain an appreciable amount of air. The average "unsaturation" of 200 samples was 9 per cent of the pore space; the highest was 22 per cent. They also have shown that the relationship between permeability and non-capillary porosity is improved when the noncapillary porosity is corrected for unsaturation. They mentioned that "theoretically, unsaturated pores would be expected to decrease the permeability of the soil to water."

Several writers have mentioned, in connection with laboratory determinations of permeability, that care must be exercised to avoid trapping air in the soil pores, and many have stressed the desirability of using upward-flow permeameters for this reason. In some instances, special precautions are taken to avoid formation of air bubbles within the soil during the test, such as using de-aired water, or heating the water to above room temperature so that there is a decreasing temperature gradient through the sample during the permeability test.

PERMEABILITY EQUATIONS AND UNITS

Permeability may be defined as the rate at which a fluid passes through a porous medium of unit area under unit gradient. The simplest expression is the "Darcy" coefficient of permeability (10), defined by the equations:

$$Q = \frac{PAH}{L} \quad (1)$$

or

$$q = P \frac{dh}{dl} \quad (2)$$

In equation (1), Q is the flow (volume per unit time), P is the "Darcy" permeability coefficient, A is the cross-sectional area of the soil column, H is the

difference in head at the two ends of the soil column, and L is the length of the column. In equation (2), q is the flow per unit area, which is the velocity of a solid water column, and $\frac{dh}{dl}$ is the hydraulic gradient, or decrease in head per unit length of column. The "Darcy" coefficient of permeability, P , is a proportionality factor which has the dimensions of velocity, i.e., LT^{-1} . In this paper P is referred to as the "permeability." It is an inverse function of the viscosity of the fluid, and where temperature variations occur, it is customary to correct to a constant temperature by multiplying the actual permeability by the viscosity ratio $\frac{\mu}{\mu_s}$, where μ is the viscosity of the fluid at the temperature at which the determination is made, and μ_s is the viscosity at a standard temperature, usually taken as 20°C. (68° F.). Such corrections may introduce errors; this point is discussed later.

Some investigators (7, 10) prefer to break down the permeability coefficient P into its more fundamental constituents. They have shown that for non-colloidal materials P is theoretically a function of the square of the particle diameter and is proportional to the acceleration of gravity and the density of the fluid, and inversely proportional to the viscosity of the fluid [i.e., $P = f\left(\frac{D^2 g \rho}{\mu}\right)$].

Although various combinations of these factors can be used as the permeability unit, P seems to be the most easily visualized, and can be most readily applied to practical problems.

When the permeability of a soil is determined in the laboratory, the soil is packed in a cylinder of uniform cross section, being supported on a screen, a porous disc, or a highly permeable material such as sand. The flow may be upward, downward, or horizontal. If the flow is upward, a low hydraulic gradient must be used, or a support over the soil column is necessary to prevent it from rising as a result of the pressure from below. If a constant water level is used the permeability can be computed from the equation:⁴

$$P = \frac{QL}{AH} \quad (3)$$

When the water level is allowed to fall in the supply reservoir (variable-head permeameters) the permeability is calculated from the equation:

$$P = \frac{aL}{AT} \ln \frac{H_1}{H_2}, \quad (4)$$

where a is the area of the water supply reservoir, A is the area of the soil column, L is the length of the soil column, H_1 is the head at the start of the test, and H_2 the head at time T .

⁴ For convenience, permeabilities reported in this paper are expressed in centimeters per hour (milliliters per square centimeter per hour) for a hydraulic gradient (H/L) of unity.

PROCEDURES AND RESULTS

Experimental work carried out in this laboratory has shown that air is entrapped in the soil regardless of how the soil is first wetted, and that the increase in permeability obtained during the second phase of the tests is due to the gradual elimination of this air. With downward flow, the air is dissolved gradually by the water passing through the soil, and successive soil layers become freed of air from the top downward.

Ordinarily the maximum permeability occurs at about the time the air is eliminated from the soil column. The rate at which the air is removed depends upon the permeability of the soil, the capacity of the water to absorb additional air, and the amount of air present in the soil. When the same amount of soil (200 gm.) is used in cylinders approximately 3.4 cm. in diameter, the time required to eliminate the entrapped air and reach maximum permeability has varied, with the different soils tested, from 3 to 53 days. The volume of leachate has varied from about 1 to more than 30 liters, corresponding to a depth of water of about 100 to more than 3,000 cm. For soils of low permeability, the time required is considerably longer. Some tests have been continued for 2 months without reaching a maximum permeability. One 3-foot soil column studied by Fireman⁵ required a year to reach maximum permeability.

Tests have been made with various types of water, including tap water, distilled water, mixtures of tap water and distilled water, and solutions of CaCl_2 and CaSO_4 . Although the permeability of the soil is affected by the composition and concentration of the water, the permeability-time curves are similar in shape. That is, the permeability first decreases, then increases, and later decreases again.

Most of the permeability tests have been carried out in glass percolation tubes arranged as shown in figure 1. The soils are air-dried and screened (1 or 2 mm.) and 200 gm. of soil is poured into the percolation tube through a 14-mm. glass tube which is slowly raised and rotated to distribute the soil evenly in the percolation tube. The soil is settled by dropping the tube on its point on a soft-wood block a given number of times through a height of about 2.5 cm. The length of column of soil is carefully measured, and the apparent density of the air-dry soil is calculated.

Four wetting procedures have been used: (1) The tubes are set in beakers of water and allowed to stand (usually overnight) until the soil is completely moistened by capillarity. (2) Water is applied to the bottom under a head greater than the length of the soil column. The flow is reversed after a small amount of water has passed through the soil. (3) Water is applied directly to the surface of the dry soil, the air being displaced through the lower end of the tube. (4) The tubes of dry soil are evacuated with an aspirator and are moistened from below while under a vacuum of about 29 inches of mercury. When wetted in this manner very little air is entrapped in the pores of the soil. Ordinarily the first procedure is used.

⁵ Fireman, M. The effect of saline irrigation waters upon the permeability and base status of soils. 1943. [Unpublished doctor's thesis. Copy on file Library, Univ. Calif., Berkeley.]

The volume of percolate is measured, usually once or twice a day, and the permeability calculated from equation (3). The temperature of the room is maintained approximately constant (24 ± 0.5 C.). No corrections have been made for temperature differences.

Effect of entrapped air

Careful observations were made of the appearance of the tubes when the increase in permeability was first thought to be due to the gradual elimination of entrapped air. These observations indicated that air was present at the beginning of the test, and that it gradually disappeared, beginning at the top of the tube. Maximum permeability occurred at about the time air was no longer

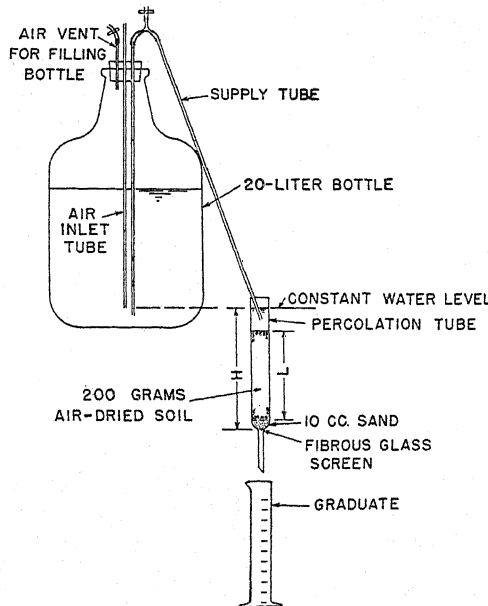


FIG. 1. ARRANGEMENT OF APPARATUS FOR SOIL PERMEABILITY TESTS

visible. As a result of these observations the following experiment was performed.

Three soils, which were being leached with a solution of CaCl_2 (5 m.e. per liter), had already passed their maximum permeability. The water supply for two tubes of each soil was shut off, and a tension of about 100 cm. of water was applied to the bottom of the percolation tubes. This was sufficient tension to draw air through the soil. One tube of each soil was then wetted from below under a low head and allowed to stand until the water covered the soil to a depth of about 1 cm. The other tubes were held for 2 days, and then water was added directly to the surface. In all cases the permeability was low at the start and increased for about 3 days. No difference could be ascribed to the method of wetting. The permeability-time relations for three of the tubes are shown in figure

2 The Superstition sand was wetted from the top, and the Hesperia sandy loam and Altamont clay loam were wetted from below under a low head.

To obtain further evidence, six tubes of Hesperia sandy loam were packed in the usual manner, and two of them were wetted under a vacuum of about 29 inches of mercury, two were wetted by capillarity from the bottom, and two were started by adding water directly to the surface of the dry soil. They were leached with tap water, which contained about 3.5 m.e. of mixed salts per liter, 50 per cent of which were sodium salts on a chemically equivalent basis. The result of this test is illustrated in figure 3, only one tube of each treatment being shown to avoid confusion. Where the air is eliminated by evacuating the soil and wetting it in the absence of air, the permeability is a maximum at the beginning of the test and decreases gradually.

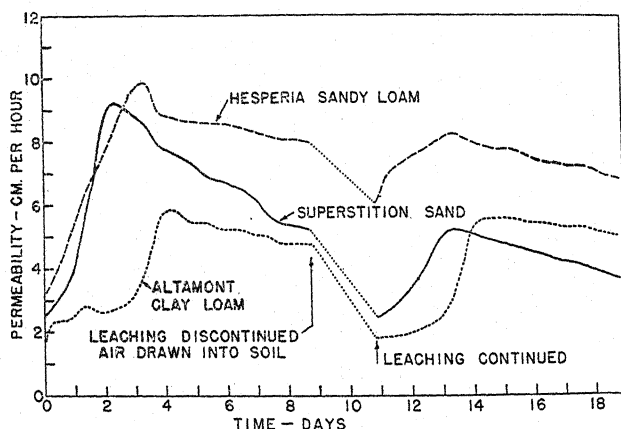


FIG. 2. PERMEABILITY CURVES FOR THREE SOILS FOR WHICH THE WATER SUPPLY WAS INTERRUPTED AND AIR DRAWN INTO THE SOIL

These soils were leached with a solution of 5 m.e. CaCl_2 per liter

Another test was conducted to determine the amount of air entrapped and the effect of variations in density upon the permeability and the air entrapment. Eighteen tubes were filled with Hesperia sandy loam, which was then compacted to different apparent densities by varying the number of impacts from 2 to 256 in geometric progression. Variations in apparent density from 1.31 to 1.47, air-dry soil basis, were obtained. The lowest densities increased to 1.35 during the test. Several additional tubes were packed to densities of about 1.40. The tubes were weighed and then set in beakers of water, wetted by capillarity, and allowed to stand in water overnight. The tubes were again weighed, and at the conclusion of the test they were weighed a third time. The difference in weight at the beginning and end of the test is an approximate measure of the pore space initially occupied by air and subsequently by water. The relationship between the percentage of pore space initially occupied by air and the relative increase in permeability, as indicated by the ratio of the maximum to previous minimum permeability ($P_{\text{max.}}/P_{\text{min.}}$), is shown in figure 4. There appears to be a good

correlation between the amount of entrapped air and the relative increase in permeability when the air is eliminated.

Tests have also been made on cylinders of soil with manometer connections on the side, so that the head loss for different sections of the column can be determined. Considering each section of column independently, we find that the permeability of the upper section first increases to a maximum, a short time later

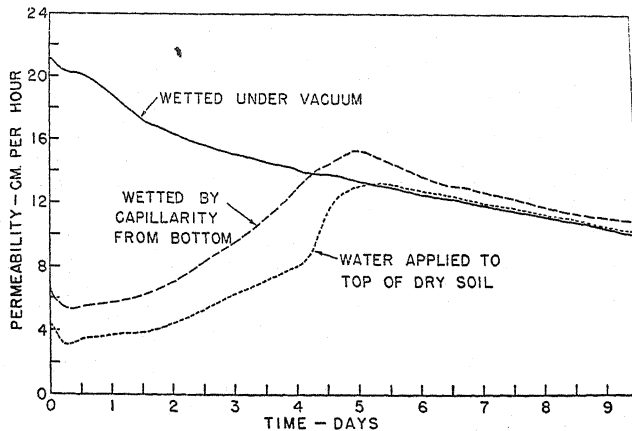


FIG. 3. EFFECT OF DIFFERENT METHODS OF WETTING ON PERMEABILITY CURVES FOR HESPERIA SANDY LOAM

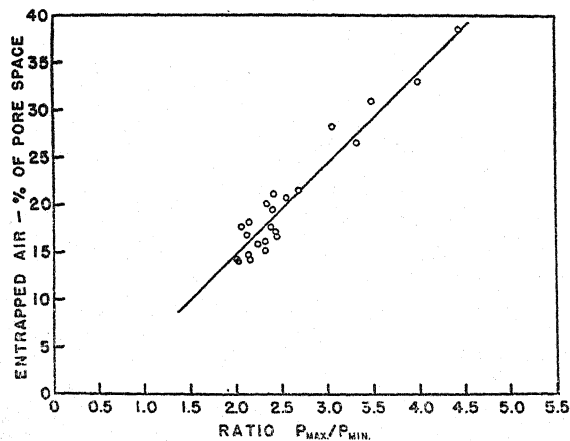


FIG. 4. RELATION BETWEEN PERCENTAGE OF ENTRAPPED AIR AND RELATIVE INCREASE IN PERMEABILITY WHEN AIR IS DISSOLVED

the second section reaches its maximum, and so in turn each section increases to a maximum, then decreases. The results of a test on a small cylinder with four manometer connections, packed with Hesperia sandy loam, are shown in figure 5. This soil column was wetted from below under a low head which was maintained until the soil surface was covered to a depth of about 1 cm.

A number of tests have been made on undisturbed soil cores 5 inches in diam-

eter and about 3 feet long. These cores are held in a pipe with seven manometer connections 6 inches apart. These cores are first wetted from the bottom under a low head and enough water is allowed to pass upward to cover completely the surface of the soil. Water is then applied to the surface, and the tests are made with downward flow. Invariably these cores exhibit the same characteristic curves, although the permeability of the soil at different horizons varies considerably.

Pressure and temperature effects

Where air is present, the volume occupied by it will depend upon the pressure and temperature, and therefore, the permeability might be expected to vary with both of these factors. Fireman⁵ noted that permeabilities determined with the

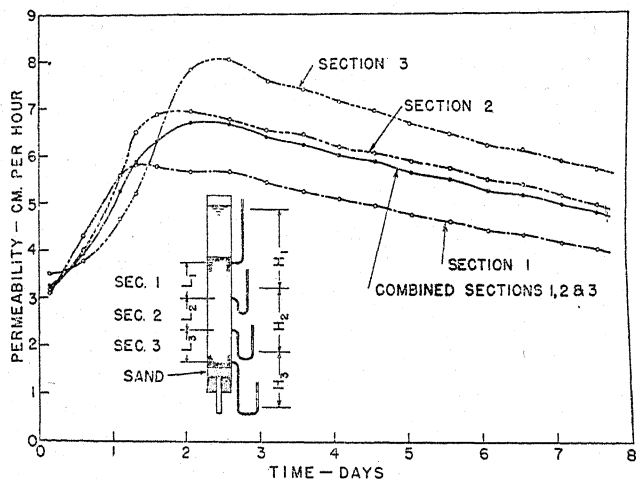


FIG. 5. PERMEABILITY-TIME RELATIONS FOR THREE SECTIONS OF A SOIL COLUMN

The permeability of the top section is a maximum on the second day, the middle section reached its maximum later the same day, and the bottom section its maximum about the end of the third day.

variable head technique decreased as the effective head decreased. Since the volume of air would increase as the pressure in the soil decreased, this might account for a decrease in permeability. Careful tests were made on two tubes of soil, using a 50-ml. burette as the supply reservoir. One tube contained soil with an appreciable amount of entrapped air, and the other had been leached under a constant head for sufficient time to eliminate the trapped air. The burette was carefully calibrated to determine the mean diameter for each section, and precautions were taken to avoid errors in measurements. Time intervals for the water level in the burette to drop between fixed graduations were made with an electrical timer reading to 0.1 second. The results are shown in figure 6. The permeability of the soil containing entrapped air decreased as the head dropped, whereas that of the saturated soil remained essentially constant. The small

variations are attributed primarily to slight errors in timing and reading the burette.

Tests on undisturbed cores with side manometers under variable temperature conditions indicated that arise in temperature caused an increase in head loss in the sections of soil containing entrapped air and a corresponding decrease in head loss in the sections from which the air had been eliminated. When a soil contains entrapped air, a change in temperature causes a change in volume of the air, and a change in viscosity of the water. These effects are opposed and therefore tend to be compensating. When permeabilities are corrected to a standard temperature on the basis of the viscosity ratio, they are actually overcorrected if air is present in the soil. This is in agreement with the findings of Fireman (4).

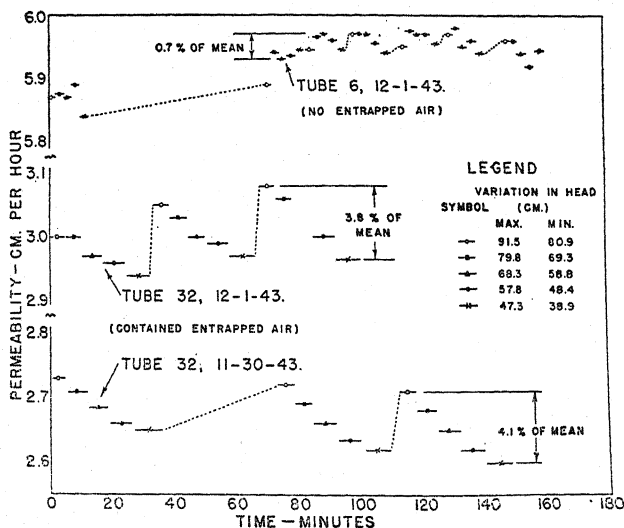


FIG. 6. EFFECT OF ENTRAPPED AIR ON PERMEABILITY DETERMINATIONS WITH VARIABLE-HEAD TECHNIQUE

Each point represents a separate determination during which the water level in the supply reservoir dropped from the maximum to the minimum head (H_1 to H_2) as given in the legend.

DISCUSSION AND CONCLUSIONS

Air entrapped in the soil upon wetting appreciably lowers the permeability. As this air dissolves, the permeability increases and reaches a maximum at about the time the air is no longer visible. The relative increase from the previous minimum permeability to maximum permeability has been found to vary widely. For Hesperia sandy loam, on which most of the tests reported here were made, this relative increase ($P_{max.}/P_{min.}$) ranged from about 2.0 to 4.5; for other soils tested it has varied from 2 to 40. Tests with distilled water have generally given the lowest ratios. No method of wetting the soil which will eliminate air entrapment has been found, except wetting under a vacuum. This is a difficult

and tedious procedure, and for some soils it apparently causes a breakdown in structure and results in much lower final permeabilities than are obtained when the soils are wetted in the usual manner. Capillary forces predominate at the wetting front, and once the soil is wetted, air present in some of the pores is completely immobilized and must be dissolved before it can be removed. Upward flow through the soil provides no assurance that air will be eliminated.

In one test, the initial permeability was 0.64 cm. per hour. This gradually decreased to a minimum of 0.117 cm. per hour on the tenth day, after which it increased slightly and then remained nearly constant until the fortieth day, when it began to increase more rapidly, reaching a maximum of 4.64 cm. per hour on the fifty-third day. The relative increase was $4.64/0.117 = 39.6$. A total of 17.7 liters of water passed through this soil sample before the maximum permeability was obtained. This corresponds to a depth of 1940 cm. of water. Only 130 ml. of water passed through another soil in 50 days. A very long period of time would be required to dissolve the entrapped air in this soil unless a different technique was used.

Caution should be exercised in applying short-time laboratory permeability determinations to field problems, especially if under field conditions the soil was continuously submerged and air was not present or would be eliminated by continuous percolation. Examples of such problems are ground-water flow, soil drainage, flow through canal linings, and flow through dams and embankments. The effect of entrapped air on permeability studies for such purposes has generally been overlooked. Many such tests are made on materials of low permeability where very long time periods would be required to eliminate air and reach maximum permeability.

SUMMARY

When soils packed in cylinders for laboratory permeability determinations are wetted, some air is trapped in the soil, regardless of whether the water is applied from the top, from below by capillarity, or under a head.

A means of avoiding this air entrapment is to evacuate the dry soil and wet it in the absence of air. For some soils, this method of wetting greatly reduces the final permeability obtained.

Upward flow of water in the permeameter is no assurance of air elimination.

Having once become immobilized, this entrapped air can escape only by dissolving in the water.

Entrapped air causes a large reduction in permeability compared with completely saturated soils. In some instances an increase of more than 30 times the previous minimum rate has been obtained with the elimination of this air.

The presence of air in the soil results in permeability values being affected by variations in pressure and temperature. The increase in volume of entrapped air with increase in temperature results in a relative decrease in flow, which partly compensates for the increase in flow due to the decrease in viscosity of the water.

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THE CHEMICAL COMPOSITION OF EARTHWORM CASTS¹

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Many years ago Gilbert White,³ and later, Darwin (2) stressed the value of earthworms to agriculture, and agronomists and foresters as well as many practical farmers and gardeners have recognized the improvement in the physical condition of the soil brought about by these inhabitants. Little has been done, however, to exploit the idea or to "put the worms to work" on any extensive scale until recently. A number of farmers have adopted what is called "earthworm tillage" or "biodynamic farming," the terms not being exactly synonymous but referring to practices which have some features in common. The reported successes of these farming methods have prompted the study of the properties of worm casts in comparison with the soil mass as a whole. No effort was made to obtain quantitative measurements of the amount of cast material thrown up in a year, although a rough estimate was made of the quantity present on the field at the time of sampling.

REVIEW OF LITERATURE

Although several workers have investigated the activities and the benefits of earthworms, only a few data on the composition of the casts have been published. Darwin (2) devoted a whole book to the subject of earthworms but did not include any such data. Hensen (3) found that loss on ignition of worm excrement lining the burrows was 3.3 to 5 per cent, compared with 2.3 per cent for the unworked soil. He also mentioned that Müller reported 24 to 30 per cent loss on ignition for worm excrement in contrast to about 8 per cent for soil. Salisbury (9) found that worm casts had a higher organic matter content than the soil in six cases out of eight. He also reported that the reaction of the casts was usually more nearly neutral than was that of the original soil. Similar findings have been reported by Robertson (7) and are shown in the data of Puh given below. Blanck and Giescke (1) found a marked increase in the nitrifying power of three different soil types as the result of earthworm activity. Earthworm casts collected from cut-over land on two soil types had higher base-exchange capacities,

¹ Contribution from the department of soils, Connecticut Agricultural Experiment Station, New Haven, Connecticut.

² Associate in forest soils and associate agronomist, respectively.

³ Russell (8) quotes the following from Gilbert White, published in 1777: "Worms seem to be the great promoters of vegetation, which would proceed but lamely without them, by boring, perforating, and loosening the soil, and rendering it pervious to rains and the fibers of plants, by drawing straws and stalks of leaves and twigs into it; and, most of all, by throwing up such infinite numbers of lumps of earth called worm-casts, which, being their excrement, is a fine manure for grain and grass . . . the earth without worms would soon become cold, hard-bound, and void of fermentation, and consequently sterile."

organic matter, and nitrogen contents than did the unworked soil mass, according to Powers and Bollen (5). They discovered that barley grown in pots produced much higher yields when earthworms were present than when the soil was free of worms.

Robertson (7) has shown that earthworms secrete calcium carbonate concretions in their calciferous glands. Secretion can take place under acid, neutral, or alkaline conditions, provided the worms have access to material containing calcium. He points out, however, that these concretions, which are excreted in the casts, do not affect the reaction of the casts in the least; it is rather the secretions of the gut wall which are responsible for changes in the reaction of the casts. When worms were kept on filter paper or in acid peat, formation of calcite concretions ceased after a week or 10 days.

Stöckli (10) studied the effect of earthworms on the soil in ten different places including garden, meadow, and forest soils. He found great variations in their activity from place to place and from season to season. Temperature and moisture were all important; geological origin of the soil was of no consequence. In comparison with the undisturbed soil, the casts and the linings of the tunnels had, in general, higher pH and loss-on-ignition values, higher content of humus soluble in 30 per cent H_2O_2 , and higher bacterial count.

Using a noncalcareous loamy clay, not ordinarily occupied by worms, with which were mixed 1 part calcareous sandy soil to 9 parts of the loamy clay, and finely cut leaves and stems of *Lactuca sativa*, Puh (6) introduced earthworms (*Pheretima bucculenta*) and left them for 2 months. At the end of this time the casts covered virtually the whole surface. Her analyses of the soil and of the worm casts at the end of this period were as follows:

	Parent Soil	Worm Casts
pH (noncalcareous loamy clay).....	6.2	6.8
pH (noncalcareous loamy clay, with calcareous sand)....	6.4	6.7
pH (calcareous loamy clays).....	8.5	7.4
	7.8	7.5
	8.0	7.2
Base capacity per 100 gm.....m.e.	21.0	25.5
Exchangeable calcium (CaO) per 100 gm.....m.e.	17.8	17.8
Available phosphorus.....p.p.m.	37.3	53.9
Available potassium.....p.p.m.	193.0	294.0
Ammonia nitrogen.....p.p.m.	33.0	49.0
CaO.....per cent	1.95	2.37
Total nitrogen.....per cent	0.054	0.151
Organic matter.....per cent	1.20	1.52

Lindquist (4) reports that earthworms increase nitrate production not only by mixing humus with mineral soil and stimulating bacterial activity but also through the decomposition of their own bodies.

AREAS SAMPLED

To obtain more complete data than have been published heretofore, to the knowledge of the writers, samples of casts and of the surrounding soil mass were

collected in the fall of 1942 from both field and forest and were subjected to rather complete analysis.⁴ The field samples were obtained in a field of sorghum and soybean stubble and young sweet clover on Earthworm Tillage Farms No. 1⁵, in North Stonington, Connecticut. The "earthworm tillage" consists essentially in working the stubble and other plant debris into the upper 4 or 5 inches of soil by means of disk and spring-tooth harrows, rather than plowing under in the conventional manner. Everything possible is done to supply food for the worms in order to increase their number. The field, of approximately 4 acres, was being pastured by ten steers and two milk cows. The soil is principally Hinckley gravelly loam, and the higher portion is classed as belonging to the Gloucester or Plymouth series. Samples were collected at 5-pace intervals along six lines across the field, and each group of line samples was composited into one sample. In each case three kinds of material were taken; first, earthworm casts; second, the adjoining soil mass to a depth of 6 inches; and third, soil at the 8-16-inch level.

The forest soil samples, obtained in four separate areas, consisted of casts; A₁ horizon (nearby top $\frac{1}{2}$ to 1 inch of soil, not casts); A₃ horizon ($1\frac{1}{2}$ to 8-inch layer consisting of the remainder of A and, in some cases, a part of the B horizon); and B₁ horizon (8 to 20 inches, more or less). Locations and descriptions of the areas are as follows:

I. Mt. Carmel State Park, Hamden. Holyoke stony fine sandy loam. Mixed hardwoods, principally oak with maple and dogwood. Samples were taken at edge of timber just in the open. Casts were numerous and well defined. (In the woods, casts prevailed, but it would have been difficult to find unworked material.)

II. Middletown, private property. Southington stony fine sandy loam. Principally white oak, with black oak, hickory, sugar maple, and other species. Casts were so numerous it was difficult to be sure of unworked soil. (Subsequent analyses, however, showed a marked difference in properties of the casts as compared with the surrounding soil mass.)

III. Meshomasic State Forest, Portland. Hinsdale stony fine sandy loam. Mixed hardwoods consisting principally of red oak, chestnut oak, white oak, dogwood, and sugar maple. Abundant casts.

IV. Middlefield, private property. Southington stony fine sandy loam. Mixed hardwoods, consisting of white, red, and chestnut oaks, hickory, sugar maple, dogwood, sassafras, and hemlock. Casts were abundant.

Quantitative measurements of the number of casts produced throughout the year or of the number of earthworms were not attempted, nor was identification of the worms as to species. A rough estimate indicated that, at the time of sampling, the casts in the field numbered approximately three to the square foot and weighed 2 ounces apiece, which amounted to about 129,000 per acre and a weight of 16,000 pounds.

RESULTS

Data pertaining to the analyses of the casts and soil from the cultivated field are given in table 1. In most cases agreement between samples from several

⁴ Field samples were collected by H. G. M. Jacobson and E. J. Rubins; those from forested areas, by H. A. Lunt and D. B. Downs. Most of the analyses were made by Mr. Rubins.

⁵ Property of Christopher M. Gallup.

parts of the field was good, and differences between horizons were considerably greater than were differences between samples from the same horizon. In nearly all cases the casts showed higher values than the 0-6-inch layer, which in turn were higher than those of the 8-16-inch depth. Greatest differences were found in available phosphorus and exchangeable potassium and magnesium, the in-

TABLE 1
Properties of earthworm casts and of soil from cultivated field
Values given are means of six samples* with standard deviations

	CASTS		SOIL 0-6"		SOIL 8-16"	
	Mean	SD	Mean	SD	Mean	SD
Total nitrogen.....per cent	0.353	0.023	0.246	0.048	0.081	0.011
Organic carbon.....per cent	5.17	0.24	3.35	0.48	1.11	0.16
Carbon: nitrogen.....	14.7	0.5	13.8	1.8	13.8	1.7
Loss on ignition.....per cent	13.1	0.6	9.8	0.3	4.9	0.4
Nitrate nitrogen.....p.p.m.	21.9	6.9	4.7	1.0	1.7	0.6
Available phosphorus (Truog)...p.p.m.	150	51	20.8	4.8	8.3	2.3
Exchangeable calcium.....p.p.m.	2,793	518	1,993	760	481	83
Exchangeable magnesium.....p.p.m.	492	75	162	44	69	14
Exchangeable Ca: exchangeable Mg = X:1.....	5.8	1.1	12.1	2.9	7.0	1.1
Total calcium.....per cent	1.19	0.28	0.88	0.18	0.91	0.33
Total magnesium.....per cent	0.545	0.066	0.511	0.066	0.548	0.047
Total Ca: total Mg = X:1.....	2.17	0.37	1.73	0.34	1.66	0.59
Exchangeable Ca in per cent of total Ca.....	25.6	10.8	24.4	13.0	6.1	2.6
Exchangeable Mg in per cent of total Mg.....	9.19	2.13	3.24	1.07	1.29	0.35
Exchangeable potassium.....p.p.m.	358	72	32	12.6	27	9.1
Exchangeable hydrogen...m.e./100 gm.	0.33	0.12	0.94	0.19	0.72	0.11
Base capacity.....m.e./100 gm.	4.67	0.29	3.82	0.61	1.63	0.06
Per cent saturation.....	92.9	2.8	74.1	9.6	55.5	6.1
pH.....	7.00	0.15	6.36	0.34	6.05	0.35
Moisture equivalent.....per cent	31.4	1.0	27.4	1.3	21.1	1.3
Silt†.....per cent	51.5	48.3	45.3
Total colloids†.....per cent	20.8	21.9	19.0
Clay†.....per cent	10.9	13.8	13.1
Fine clay†.....per cent	9.1	10.2	10.7

* Each sample was a composite of individual samples collected at 5-pace intervals on a line across the field. There were six lines, hence six samples.

† Composite samples from whole field.

creases in the casts over the surrounding topsoil ranging from threefold to elevenfold. Even the nitrogen, organic carbon, and total calcium figures are obviously highly significant, the differences being 35 to 50 per cent. The lower clay content of the casts may or may not be significant. The total magnesium contents of casts and of soil were virtually identical.

In the forest soils (table 2) agreement among the four profiles was remarkably

TABLE 2
Properties of earthworm casts and of soil from forested areas

PROFILE	CASTS	A ₁	A ₃	B ₁	CASTS	A ₁	A ₃	B ₁	CASTS	A ₁	A ₃	B ₁
	Total N, % (WF)*				Organic C, % (WF)				C:N			
I	0.630	0.382	0.133	0.086	14.9	6.5	2.0	1.3	23.8	17.1	14.7	15.7
II	0.630	0.292	0.106	0.039	17.4	5.3	1.8	0.6	27.6	18.0	17.1	15.9
III	0.717	0.320	0.151	0.071	16.6	6.8	2.7	1.0	23.1	21.1	17.5	14.7
IV	0.523	0.314	0.131	0.062	13.4	5.0	2.1	0.9	25.7	15.8	16.0	13.7
Av.	0.625	0.327	0.130	0.064	15.6	5.9	2.1	1.0	25.1	18.0	16.3	15.0
	pH				Loss on ignition, % (WF)				Available P (Truog), %			
I	5.41	4.75	4.48	4.60	27.6	13.6	5.8	4.8	27.4	22.3	7.8	9.4
II	5.35	4.65	4.55	4.69	32.4	11.7	3.6	2.9	19.4	9.1	5.1	3.9
III	5.00	4.43	4.71	4.82	30.2	12.6	5.6	3.0	21.3	20.9	6.8	13.2
IV	5.29	4.66	4.69	4.73	25.7	11.8	5.3	3.4	16.1	7.7	3.6	3.3
Av.	5.26	4.62	4.61	4.71	29.0	12.4	5.1	3.5	21.1	15.0	5.8	7.5
	Exchangeable Ca, p.p.m.				Exchangeable Mg, p.p.m.				Exch. Ca:exch. Mg = X:1			
I	4,280	1,183	95	111	328	109	27	26	13.0	10.8	3.5	4.3
II	5,300	844	151	200	511	153	24	69	10.4	5.5	6.3	2.9
III	3,272	224	51	46	354	69	15	12	9.2	3.2	3.4	3.8
IV	2,900	738	323	325	480	227	105	127	6.0	3.3	3.1	2.6
Av.	3,938	747	155	171	418	140	43	59	9.6	5.7	4.1	3.4
	Total Ca, % (WF)				Total Mg, % (WF)				Total Ca:total Mg = X:1			
I	1.00	0.94	0.62	0.59	0.378	0.648	0.614	0.580	2.64	1.45	1.01	1.02
II	1.05	0.58	0.51	0.47	0.591	0.691	0.530	0.555	1.78	0.84	0.96	0.85
III	1.40	1.46	1.36	1.21	0.592	0.643	0.564	0.580	2.36	2.27	2.41	2.09
IV	0.78	0.42	0.48	0.45	0.534	0.661	0.685	0.582	1.46	0.63	0.70	0.77
Av.	1.06	0.85	0.74	0.68	0.524	0.661	0.598	0.574	2.06	1.30	1.27	1.18
	Exch. Ca in % of total Ca				Exch. Mg in % of total Mg				Exchangeable K, p.p.m.			
I	42.8	12.6	1.5	1.9	8.68	1.68	0.44	0.45	293	217	35	35
II	50.5	14.5	3.0	2.3	8.65	2.21	0.45	1.24	217	151	19	12
III	23.4	1.5	0.4	0.4	5.98	1.07	0.27	0.21	247	115	43	25
IV	37.2	17.6	6.7	7.2	8.98	3.43	1.53	2.18	168	69	30	30
Av.	38.5	11.5	2.9	2.9	8.07	2.10	0.67	1.02	231	138	32	25
	Exch. H, m.e. per 100 gm.				Base capacity, m.e. per 100 gm.				% Saturation			
I	10.1	9.5	6.6	5.7	30.4	15.7	8.1	7.3	67	40	18	21
II	10.7	9.4	5.6	3.7	34.3	14.4	6.3	5.0	69	35	11	26
III	14.6	13.0	6.6	3.5	29.6	16.2	8.2	3.9	51	20	19	11
IV	10.2	9.3	5.7	4.2	27.5	13.9	7.5	5.9	63	33	24	29
Av.	11.4	10.3	6.1	4.3	30.5	15.1	7.5	5.5	63	32	18	22

TABLE 2—Continued

PROFILE	CASTS	A ₁	A ₂	B ₁	CASTS	A ₁	A ₂	B ₁	CASTS	A ₁	A ₂	B ₁
	Moisture equivalent, %				Total colloids, %				Clay, %			
I	48.4	27.4	19.9	19.0	13.0	13.0	6.2	25.2	8.8	8.2	5.6	14.8
II	61.2	31.2	18.5	15.4	17.8	18.0	7.8	31.6	10.0	10.8	4.0	22.0
III	49.6	26.8	18.1	12.6	21.6	24.2	13.0	32.0	12.8	15.6	6.6	21.6
IV	52.2	35.1	24.4	20.1	26.4	26.2	17.6	30.4	18.4	15.6	8.4	20.8
Av.	52.9	30.1	20.2	16.8	19.7	20.4	11.2	29.8	12.5	12.6	6.2	19.8

* *WF* values are on a water-free basis.

close, and differences between horizons are obviously highly significant. The higher contents of nitrogen, organic carbon, and exchangeable calcium in the casts were even more pronounced here than they were in the field soil, particularly when the A₃ horizon is considered. The A₁ and A₃ together correspond roughly to the 0-6-inch layer of the cultivated soil. On the other hand differences in available phosphorus and exchangeable potassium and magnesium were distinctly smaller than in the field soil. Total magnesium content was actually lower in the casts than in the A₁. There was no essential difference in either the total colloids or the clay content of the casts as compared with the A₁ horizon, but both were considerably lower in the A₃.

In comparison with the cultivated soil, the forest soil casts were much higher in nitrogen, carbon, exchangeable calcium, and moisture-equivalent values. The higher proportion of exchangeable calcium to exchangeable magnesium in the upper horizon of the field soil was not observed in the forest soil, nor was there any such relation between *total* calcium and *total* magnesium in either soil. The proportion of calcium that was in exchangeable form was about the same in the casts as it was in the A₁ horizon in the field soil, but in the forest soil the proportion in the casts was distinctly higher than in the A horizons. The proportion of magnesium that was exchangeable was definitely higher in the casts in both soils.

In all cases the pH of the casts was higher than in the parent soil. Nitrate nitrogen was not determined on the forest soils. Lime applied sometime in the past to the cultivated soil had raised the pH, total calcium, and, with one exception, the exchangeable calcium content of all horizons considerably above the corresponding values found in the forest soils.

DISCUSSION

Soil in which earthworms are active is invariably in better physical condition than is similar soil without earthworms. Though it is the opinion of some that the worms are present because of the favorable soil conditions, there is sufficient evidence (1, 3, 8, 10) to indicate that earthworms do very definitely improve soil structure by increasing aggregate content and porosity, thus facilitating aeration, water absorption, root penetration, and drainage. Stöckli (10) reported that casts contained no particles larger than 2 mm. in diameter and that in some cases

particle size was reduced by means of a rubbing action inside the digestive tract of the worm. Mechanical analyses of our samples showed no essential differences in the texture of casts and topsoil.

From the biological standpoint, casts have been found to contain a much larger bacterial population than the unworked soil (10).

The data on chemical properties herein reported confirm those published by Powers and Bollen (5) and by Puh (6), with one notable difference in Puh's work. She found the casts to be markedly higher in total calcium but not in exchangeable calcium. No explanation for this difference was given.

Only a cursory examination of the data is needed to show the higher fertility status of the casts. What is the explanation? Is it due to substances brought up from the subsoil, or can it be attributed to direct action of the worms on the soil material? To answer these questions, it is necessary to examine the habits of earthworms. They make their tunnels, in part, by pushing the earth away on all sides, but mostly by swallowing it and depositing the excrement at the surface. In dry or cold weather they retire to considerable depth—4 to 6 and even 8 feet. In favorable weather they are active in the top 6 or 8 inches of soil. Their food consists of plant and animal remains on the surface and in the upper layers of the soil; and apparently some nutriment is obtained from the soil itself. In the light of these facts it is interesting to speculate as to what would happen in an inverted profile, i.e., with the A and C horizons reversed. The fact that worm casts are less acid (or less alkaline in alkaline soils) than the soil even where the worms are confined to the surface soil (6, 9), shows what the change in reaction is not dependent upon the transporting of less acid (or less alkaline) subsoil to the surface. Burrowing in the subsoil is done only to provide living quarters during unfavorable weather. It would appear, therefore, that the amount of subsoil carried to the surface is relatively small. If the subsoil is calcareous, the amount of such material brought to the surface might, over a long period of time, be sufficient to increase the calcium (and perhaps magnesium) content of the surface soil. Likewise, if the subsoil contained a higher concentration of any other material, it might influence the composition of the surface soil.

The main benefit, chemically (and biologically), of earthworm activity is the digestion of plant material and its intimate mixing with mineral soil. The concentration of the principal plant-food elements (except K) in the plant is considerably higher than it is in the soil. For example, in southern New England, forest tree leaves contain in the neighborhood of 0.5 to 2.5 per cent N, 0.1 to 0.5 per cent P, 0.6 to 2.0 per cent K, and 1 to 4 per cent Ca; whereas the amount in the soil averages about 0.2, 0.08, 1.5, and 0.5 per cent respectively, only a fraction of which is available to the plant. Both the mechanical mixing and the action of digestive secretions favor the decomposition of the organic matter and of soil minerals. The resultant product contains a lower concentration of plant-food than the plant residues but a higher concentration than the soil. The process may be likened to the consumption of grass, hay, and grains by cattle and the subsequent return of the manure to the soil,—with this difference, however. The cattle (or the milk from cows) are sold from the farm, resulting in net loss to the

soil of a certain amount of plant-food. Also, some losses occur in the manure before it is incorporated with the soil. The earthworm, on the other hand, dies in the soil and its decomposed body returns plant-food to the soil without loss. It has been found that the increased nitrification that takes place when earthworms are introduced into the soil is due, in part at least, to the decomposition of their own bodies (6, 8). Russell (8) reported the nitrogen content of worms to be 1.5 to 2.0 per cent or about 10 mgm. of N per worm.

That yields may be increased by the presence of earthworms has been demonstrated in pot culture studies (5, 8). On a field scale, however, no accurate quantitative comparisons have been made, to the knowledge of the writers. Inasmuch as any practice that favors earthworm activity is also favorable to plant growth, it is extremely difficult in the field to determine to what degree the worms are responsible for any increase in yields or improvement in quality of the crop. Obviously one should avoid any practice that would materially reduce earthworm activity. Whether or not it is practicable deliberately to increase the worm population is another question and one which still lacks an answer.

SUMMARY

Samples of earthworm casts and of unworked soil from several depths were collected from a cultivated field and from four forested areas and subjected to chemical and mechanical analyses.

At the time of sampling, the field soil contained approximately three casts to the square foot, averaging 2 ounces each, or 16,000 pounds to the acre.

In the field soil, casts contained less exchangeable hydrogen and a lower clay content than the 0-6-inch layer; but the casts had higher pH values and were higher in total and nitrate nitrogen, organic matter, total and exchangeable calcium, exchangeable potassium and magnesium, available phosphorus, base capacity, base saturation, and moisture equivalent. Total magnesium was about equal in all samples.

Forest soil samples showed similar but even more striking results. Forest soil casts were higher in nitrogen, organic carbon, and exchangeable calcium, and had a higher moisture equivalent than the casts from the field soil.

These changes in composition as the result of earthworm activity are due chiefly to the intimate mixing of plant and animal remains with mineral soil in the digestive tract of the worm and to the action of digestive secretions on the mixture. That earthworms are beneficial to the soil has been established beyond a doubt. Conditions favorable to the worms, however, are at the same time favorable to plant growth, and quantitative measurements under field conditions of the part the worms play in crop production have not as yet been obtained.

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THE INFLUENCE OF TEMPERATURE ON THE MICROFLORA OF THE SOIL

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The number, kind, and physiological efficiency of the microflora of a soil are the resultant of numerous factors. The physical, chemical, and biological properties of the soil together with the interaction of climate, season, moisture, and temperature are constantly at work. The first six factors have received considerable attention from research workers, but the influence of temperature on the enduring microflora of the soil has been studied but little.

The number of bacteria in the soil varies considerably with the season of the year. Cutler, Crump, and Sandon (6) noted the general level of numbers to be highest in spring and autumn. Wakesman (26), on the other hand, found that maximum bacterial numbers varied with different soils throughout the year; no two soils showed their maximum bacterial content at the same sampling. Russell (22) reported that numbers of soil bacteria are somewhat unresponsive to changes in temperature within the limits of trophic life. He found an hourly fluctuation, and numbers showed no relationship to temperature or moisture content. Cutler and Crump (7, p. 18) concluded that increased temperature tended to lower the numbers, whereas increased moisture content appeared to raise them. Conn (5) found that freezing the soil greatly increased the numbers of bacteria, a result never adequately explained. Russell and Hutchinson (21), using soils stored under carefully controlled conditions at temperatures of 5-12°, 20°, 30°, and 40°C., found that the numbers of bacteria in untreated soil had in the main a downward trend as the storage temperature increased.

Investigations of the influence of temperature on ammonification are limited in scope. Marchal (18) worked with solutions and found that only traces of ammonia were produced from 0° to 5°C., with a maximum production at 30°C. According to Panganiban (20), ammonia production occurs between 15° and 60°C., and he considered thermophilic microorganisms to be very active at higher temperatures.

More extensive studies have been made on the influence of temperature on nitrification. Deherain (8) found nitrification very slow at 5°C. Hutchinson (13) reported the optimum temperature for nitrification in Pusa soil to be 35°C. He found no nitrate produced at 40°C., and nitrification did not take place in soil which had been kept at 40°C. and later reduced to 30°C. Von Bazarewski (1) reported the most favorable temperatures in artificial media for nitrification to be between 25° and 27°C., or about 10° lower than in pure cultures. King and Whitson (14) found an accumulation of 120 pounds of nitric nitrogen per acre at 1°C.; 150 pounds per acre at 9°C.; 329 pounds per acre at 20°C., and 747 pounds per acre at 35°C. Löhnis and Green (17) found that temperatures between 30° and 35°C. suppressed the conversion of nitrites into nitrates. The optimum for

nitrification they found to be between 22° and 28°C. Schlosing and Muntz (23) reported that nitrate formation proceeded very slowly at 5°C; at 20°C. it was appreciable; and at 37°C. it reached its optimum. Guistiniani (11) considered the minimum for nitrate formation to be 4°C. and the optimum between 35° and 37°C. The higher temperature is the one Boullanger and Massol (3) considered optimum. It is thus evident that there is a wide divergency of views as to the optimum temperature and little is known concerning the enduring influence of temperature on nitrification.

The influence of temperature on nitrogen fixation has been rather extensively studied. Berthelot (2) early recognized that the biological gain of nitrogen in soils is dependent upon a suitable temperature, between 10° and 40°C. Krezemeniewski (16) found the optimum temperature for *Azotobacter* to be 28°C., and the limits to lie between 9° and 33°C. Walton (27) observed in Indian soils that fixation was usually greater at 30° than at 20°C.; however, in six cases out of seventeen he found it to be highest at 20°C. According to Heinze (12), nitrogen fixation is most active between 20° and 30°C., but appreciable quantities are fixed at 8° to 10°C. Koch (15) obtained fixations of 3, 11, and 15.5 mgm. of nitrogen in 100 gm. of soil when incubated with a carbohydrate at 7°, 15°, and 24°C. respectively. Traaen (25) using a loam soil with optimum moisture obtained nearly as great a fixation at 13° as at 25°C.

There is some evidence that the optimum temperature for the various biological activities is influenced by the climate of the region. Tandon and Dhar (24) found the optimum temperature for nitrate producers in tropical soils to be 35° as against 25°C. in temperate climates. Mischustin (19) observed that optimum temperatures for soil bacteria depend upon the soil from which the organisms were isolated; bacteria from soils of colder climates were capable of growing at lower temperatures than bacteria from soils of warm climates.

It is evident from the preceding summary that the numbers and activities of the microflora of a soil are dependent upon the incubation temperature of the soil, but specific information is lacking as to whether the microflora becomes acclimated to temperature and is more or less permanently modified by it. A knowledge of the enduring effect of temperature on the microflora of the soil is important. Farmyard manure applied to a soil may add new microorganisms and modify its temperature. Summer fallowing enables soils to reach comparatively high temperatures during the summer months (4). If, because of these and other factors, a thermophilic microflora results, and the organisms find their way from the beet into the sugar and then into processed fruits and vegetables, new problems in the canning industry are raised. Hence this work was planned to answer the question: What influence has storage of soils for months at varying temperatures on the numbers of microorganisms and on the ammonifying, nitrifying, and nitrogen-fixing activities of soil? Thus to future work is left the problem of thermophiles and psychrophiles in such soils.

EXPERIMENTAL METHODS

Four different soils were sampled, air-dried, and passed through a 20-mesh sieve. Each soil sample was divided into four subsamples as follows: soil I—1, 1A,

1B, and 1C; soil II—2, 2A, 2B, and 2C; soil III—3, 3A, 3B, and 3C; and soil IV—4, 4A, 4B, and 4C. All subsamples were carefully weighed into pans having a diameter of 11 inches and a depth of $3\frac{1}{4}$ inches. Each pan contained 2,000 gm. of soil (dry basis) which filled it to a depth of approximately 2 inches. The water-holding capacity of each sample was determined, and sufficient water added to bring the soil to 50 per cent of its capacity. Subsamples 1, 2, 3, and 4 were stored in an incubator at 10°C.; 1A, 2A, 3A, and 4A, at 20°C.; 1B, 2B, 3B, and 4B, at 30°C.; and 1C, 2C, 3C, and 4C, at 40°C. Temperatures were checked in each incubator with recording thermometers and found to remain constant. Moisture in soils kept at 40°C. was checked every other day and brought up to original weight; that of soils at 30°C., twice a week; that of soils at 20°C., weekly; and that of soils at 10°C., every 2 weeks.

At the end of 6-, 12-, 18-, and 24-month storage periods the samples were removed from the pans, with the exceptions noted below, and were air-dried and then thoroughly mixed. At each period, plate count, ammonification, nitrification, and nitrogen fixation determinations were made on each subsample, and results were calculated to a dry basis. Soils stored at 40°C. showed a marked decline in their bacterial activities at the end of the 12-month period; hence this part of the experiment was terminated. Ammonification, nitrification, and nitrogen fixation determinations were made by the solution method at the end of 6, 12, and 18 months. The determinations including the plate count are described in a previous article (10). Five replicates were run on each subsoil, and the plates were incubated at 30°C. Ammonification, nitrification, and nitrogen fixation also were determined by the tumbler method (9) at the end of 24 months, when incubation was at 20° and 30°C.

As shown in table 1, the soils varied in nitrogen content from 0.07 to 0.27 per cent, and in water-holding capacity from 35 to 54.7 per cent.

RESULTS

The soil counts in millions of microorganisms at the beginning of the experiment were: clay loam 3.84, sandy loam 4.38, dark loam 10.16, light loam 3.90. Hence, as shown in table 2, there was a highly significant difference in the numbers of microorganisms developing from the dark loam as compared with any of the other soils. The other soils did not show great difference in numbers.

The average differences between means of soil stored at 10° and at 30° or 40°C. were highly significant, whereas the difference between other temperatures just approached significance.

The average mean difference in the microbiological count of the clay loam as compared with either the sandy loam or the light loam was significant and approached the highly significant point.

Hence we have within the various soils a significant difference in bacteria, a difference which is maintained until a temperature of 40°C. is reached. The change occurring at the higher temperatures must be the result of selective action and not of dormancy, as these soils still showed low counts when plated and the plates incubated at varying temperatures. This is evident from table 3, in which

are reported only the mean numbers of colonies obtained from all the soils stored at varying temperatures for 2 years and then incubated at 20° or 30°C.

The storage of these soils at 10°C. had a highly significant effect upon the numerical content of microorganisms which would develop upon synthetic glucose agar. In the soils that had been stored at 10° or 20°C. the numbers of organisms which developed when incubated at 20° and at 30°C. were very different. In soils stored at 30°C., the number had decreased, and most of the surviving organisms developed equally well at incubation temperatures of either 20° or

TABLE 1
Nitrogen content and water-holding capacity of soils

SOIL NUMBER	SOIL TEXTURE	NITROGEN	WATER-HOLDING CAPACITY PER 100 GM.
		<i>per cent</i>	<i>ml.</i>
I	Clay loam	0.16	47.7
II	Sandy loam	0.07	35.0
III	Dark loam	0.27	54.7
IV	Light loam	0.17	44.9

TABLE 2
Average number of microorganisms in soil, developing in 5 days at 30°C. on synthetic glucose agar, determined after 6-, 12-, and 18-month storage periods

STORAGE TEMPERATURE	MICROORGANISMS, IN MILLIONS PER GRAM				
	Clay loam	Sandy loam	Dark loam	Light loam	Storage temperature mean
°C.					
10	23.10	4.01	10.83	3.81	10.44
20	7.91	3.67	9.32	2.38	5.82
30	2.92	2.35	5.16	1.56	3.00
40	1.69	1.88	2.48	1.48	1.88
Soil mean...	8.91	2.98	6.95	2.31
5 per cent level of significance for storage temperature mean.....					4.24
1 per cent level of significance for storage temperature mean.....					5.95
5 per cent level of significance for soil mean.....					4.90
1 per cent level of significance for soil mean.....					5.95

30°C. The results warrant the conclusion that the storage of these soils at various temperatures for 2 years modifies the numerical content of microorganisms which will develop on synthetic glucose agar. Hence it is highly probable that the number of microorganisms within a soil is a function of the temperature of the soil prior to its plating and that these differences are great enough to be measured by the plate method.

The ammonia production of the various soils on inoculation into peptone solution when first brought to the laboratory was: clay loam 76.3 mgm., sandy loam

91.5 mgm., dark loam 96.5 mgm., and light loam 87.5 mgm. Hence, all soils had an active ammonifying microflora but not so different as is often found in field soils. As shown in table 4, there is a highly significant difference in the mean concentration of ammonia found within the various soils after storage, however; the mean difference at the various storage temperatures is also highly sig-

TABLE 3

Mean number of colonies developing from four soils stored at different temperatures for 2 years, then plated and incubated at 20° and 30°C.

STORAGE TEMPERATURE	INCUBATION TEMPERATURE	MEAN NUMBER OF COLONIES AT INCUBATION TEMPERATURE	MEAN NUMBER OF COLONIES AT STORAGE TEMPERATURE
°C.	°C.		
10	20	1.84	2.67
	30	3.49	
20	20	0.62	0.93
	30	1.24	
30	20	0.42	0.59
	30	0.77	

5 per cent level of significance for storage temperature mean..... 0.58

1 per cent level of significance for storage temperature mean..... 0.88

5 per cent level of significance for incubation temperature mean..... 0.82

1 per cent level of significance for incubation temperature mean..... 1.25

TABLE 4

Average ammonia production per gram of soil inoculated into peptone solution, incubated at 30°C. for 72 hours, determined at intervals of 6, 12, and 18 months

STORAGE TEMPERATURE	AMMONIA PRODUCED				
	Clay loam	Sandy loam	Dark loam	Light loam	Storage temperature mean
°C.	mgm.	mgm.	mgm.	mgm.	mgm.
10	104.1	95.8	73.5	110.3	95.9
20	99.0	92.8	65.9	105.2	90.7
30	94.9	87.9	59.8	96.4	84.8
40	76.0	75.0	56.8	93.4	75.3
Soil mean.....	93.5	87.9	64.0	101.3

1 per cent level of significance for temperature mean..... 4.3

1 per cent level of significance for soil mean..... 5.9

nificant. This indicates that the amount of ammonia produced within these soils is a function of the temperature at which they have been held. The greatest concentration of ammonia was obtained in the samples that had been stored at 10°; and the lowest, at 40°C. The accumulation of ammonia at 10°C. is probably largely the result of a retarding of the processes which transform ammonia

into nitrates or proteinaceous nitrogen. On the other hand, the smaller quantities found at 40°C. may have been caused by a slowing down of ammonification, a recession of nitrification, and possibly a speeding up of synthetic reactions. Hence it may be concluded that the ammonifying powers of soils may be changed by long keeping at various temperatures, but this factor may not be sufficient to obliterate differences resulting from the chemical and physical composition of a soil.

Results of the determinations of ammonification by the tumbler method after 2 years storage are presented in table 5. There was a highly significant difference in the means of ammonia obtained from the soils stored at the various temperatures. The recovery was highest in the soils stored at 10°C. and lowest in the soils stored at 30°C. The incubation temperature likewise had a highly significant effect upon the ammonia produced. This was invariably higher at

TABLE 5

Ammonia recovered per gram from soils stored at different temperatures for 2 years and then incubated in tumblers with dried blood for 7 days

STORAGE TEMPERATURE	INCUBATION TEMPERATURE	MEAN RECOVERY OF NH_3 AT INCUBATION TEMPERATURE	MEAN RECOVERY OF NH_3 AT STORAGE TEMPERATURE
°C.	°C.	mgm.	mgm.
10	20	73.6	101.3
	30	129.0	
20	20	58.8	91.8
	30	124.8	
30	20	53.0	82.5
	30	111.9	
1 per cent level of significance for storage temperature mean.....			2.1
1 per cent level of significance for incubation temperature mean.....			2.3

30°C. than at 20°C. Hence it appears from these results that 2 years' storage at 10°, 20°, or 30°C. has so profound an influence upon the ammonifying microflora of these soils that it is not obliterated by incubation with dried blood for 7 days at 20° or 30°C.

At the beginning of the experiment the nitrifying powers of three soils—clay loam 17.3 mgm., sandy loam 17.8 mgm., and dark loam 18.0 mgm.—were not greatly different, but the light loam had a distinctly different nitrifying power, as it yielded only 6.3 mgm. of nitrates. After storage at 40°C., the nitrifying powers of all soils had been significantly decreased, as shown in table 6. There was also a lower accumulation of nitrates in the soil stored at 10°C. than in those stored at either 20° or 30°C. It may be concluded that the nitrifying powers of the soils were changed by storage for 18 months at either 10° or 40°C. Apparently 20° and 30°C. were without effect and both temperatures are equally satisfactory for the maintenance of soils at a high nitrifying power. Apparently a temperature

of 40°C. had destroyed the nitrifying microorganisms in the dark loam and the light loam, as repeated tests failed to give any nitrifying activity. This however, was not the case with the clay loam or the sandy loam.

The nitrifying powers of each of these soils were determined by the tumbler method at 20° and 30°C. at the end of two years, and the means are reported in table 7. It can be seen that the mean difference in the nitrate produced in soils

TABLE 6

Average nitrate production per gram of soil inoculated into ammonia medium and incubated at 30°C. for 21 days, determined at intervals of 6, 12, and 18 months

STORAGE TEMPERATURE °C.	NITRATE PRODUCTION				
	Clay loam mgm.	Sandy loam mgm.	Dark loam mgm.	Light loam mgm.	Storage temperature mean mgm.
10	16.7	19.2	16.5	5.7	14.5
20	18.4	19.3	18.9	13.6	17.6
30	18.2	18.4	17.1	17.0	17.7
40	15.4	10.5	0.0	0.0	6.5
Soil mean.....	17.2	16.8	13.1	9.1

1 per cent level of significance for storage temperature mean..... 2.8

5 per cent level of significance for soil mean..... 2.3

TABLE 7

Nitrate recovered per gram from soils stored at different temperatures for 2 years and then incubated in tumblers with dried blood for 21 days

STORAGE TEMPERATURE °C.	INCUBATION TEMPERATURE °C.	MEAN RECOVERY OF NO ₃ AT INCUBATION TEMPERATURE mgm.	MEAN RECOVERY OF NO ₃ AT STORAGE TEMPERATURE mgm.
10	20	34.0	29.7
	30	25.5	
20	20	30.6	28.7
	30	26.9	
30	20	39.4	38.5
	30	37.6	

5 per cent level of significance for storage temperature mean..... 11.3

stored at 10° or 20°C. and in those stored at 30°C. approached significance, but the highest nitrification occurred in soil stored at 30°C. The influence of incubation temperature upon the soils was erratic; more nitrate was produced in the soils stored at 10° and 20°C. when incubated at 20°C., but in the soils stored at 30°C. there was no significant difference between incubation at 20° and at 30°C. This tends to indicate that storage temperature has a more lasting effect upon ammonification than it has upon nitrification.

The nitrogen-fixing powers of the various soils at the different temperatures are presented in table 8.

The nitrogen-fixing powers of the various soils at the beginning of storage were: clay loam 9.2 mgm., sandy loam 10.9 mgm., dark loam 10.2 mgm., and light loam 5.9 mgm. nitrogen. The difference in the nitrogen-fixing powers of three of

TABLE 8

Average fixation of nitrogen per gram of soil inoculated into Greaves' medium and incubated at 30°C. for 21 days, determined at intervals of 6, 12, and 18 months

STORAGE TEMPERATURE	NITROGEN FIXED				
	Clay loam	Sandy loam	Dark loam	Light loam	Storage temperature mean
°C.	mgm.	mgm.	mgm.	mgm.	mgm.
10	9.4	8.1	9.5	6.7	8.4
20	10.1	8.9	9.2	6.3	8.6
30	9.2	8.6	10.1	7.9	9.0
40	7.9	5.4	7.7	6.7	6.9
Soil mean.....	9.2	7.8	9.1	6.9
5 per cent level of significance for storage temperature mean.....					0.78
5 per cent level of significance for soil mean.....					0.90

TABLE 9

Mean fixation of nitrogen per gram in soils stored for 2 years at different temperatures and then incubated in tumblers for 27 days with 2 per cent mannitol

STORAGE TEMPERATURE	INCUBATION TEMPERATURE	N FIXED AT INCUBATION TEMPERATURE	N FIXED AT STORAGE TEMPERATURE
°C.	°C.	mgm.	mgm.
10	20	5.1	5.2
	30	5.3	
20	20	9.1	9.2
	30	9.3	
30	20	8.4	8.8
	30	9.3	
5 per cent level of significance for storage temperature mean.....			0.38
1 per cent level of significance for storage temperature mean.....			0.58
5 per cent level of significance for incubation temperature mean.....			0.54
1 per cent level of significance for incubation temperature mean.....			0.82

the samples was slight, but the nitrogen-fixing power of the light loam was significantly lower than in the other soils. The storage temperature, with the exception of 40°C., had no significant effect upon the soils. These results are in accord with results obtained with alkali soils. Soil alkalies have a far-reaching effect upon nitrifiers but little or no effect on the nitrogen-fixing microorganisms.

The nitrogen-fixing powers of these soils were also determined by the tumbler method after storage for 2 years at incubation temperatures of 20° and 30°C. The mean values obtained are presented in table 9.

The difference between nitrogen-fixed by soil stored at 10° and that stored at 20° or 30°C. was highly significant. Low storage temperature has a lasting effect on the nitrogen-fixing powers of soil. The incubation temperature on the other hand, did not significantly affect the nitrogen-fixing powers. Hence the nitrogen-fixing power of a soil is a function of the storage temperature, and these results apparently bear out the conclusion that soil temperatures are high enough during a considerable period of the year to favor nitrogen fixation.

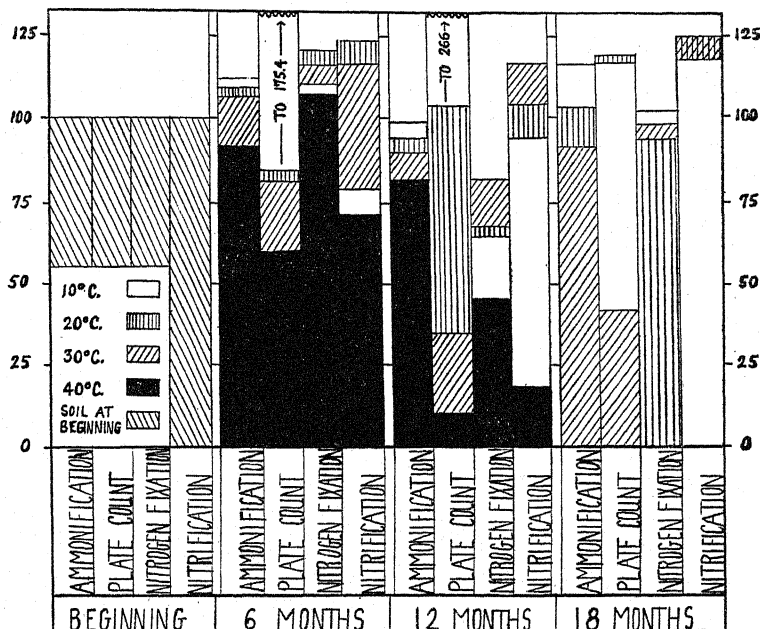


FIG. 1. PLATE COUNT, AMMONIFICATION, NITRIFICATION, AND NITROGEN FIXATION OF SOILS STORED FOR 6, 12, AND 18 MONTHS AT 10°, 20°, 30°, AND 40°C.

The various microbiological processes at the beginning of the experiment were taken as 100 per cent

The mean summarized results for number of microorganisms, ammonification, nitrification, and nitrogen fixation at the beginning of the experiment and at the end of 6-, 12-, and 18-month periods are presented in figure 1. The mean at the beginning in each process is taken as 100 per cent, and the relative percentages at the end of 6, 12, and 18 months are given. The storage of these soils at 10°C. increased the plate count, and the storage at 40°C. invariably decreased it. This also holds for ammonification. Nitrification was greatest at 20°C. at the end of 6 months, and greatest at 30°C. at the end of 12 months, but by the end of 18 months the 20° and 30° were the same. All bacterial activities were greatly restricted by the higher temperature. Nitrogen fixation was not greatly in-

fluenced by storage temperature, except at 40°C. It is interesting to note that even after storage for 18 months at 10°C. the soils are still active nitrogen fixers.

SUMMARY

Four different soils were stored for 24 months at 10°, 20°, 30°, and 40°C. and at the end of 6, 12, 18, and 24 months were analyzed for numbers of microorganisms, accumulation of ammonia and nitrates, and total gains in nitrogen.

The storage of soils at different temperatures for 24 months changed the number of microorganisms which developed on synthetic glucose agar. The greatest number developed when the soils had been stored at 10°C., and the fewest at 40°C.

The ammonifying powers of the soils tested were modified by storing for 24 months at various temperatures. The accumulation of ammonia was greatest in soils which were stored at 10°C. and least in those stored at 40°C. This difference produced by storage was so great that it was not obliterated by incubating with dried blood for 7 days at 20° or 30°C.

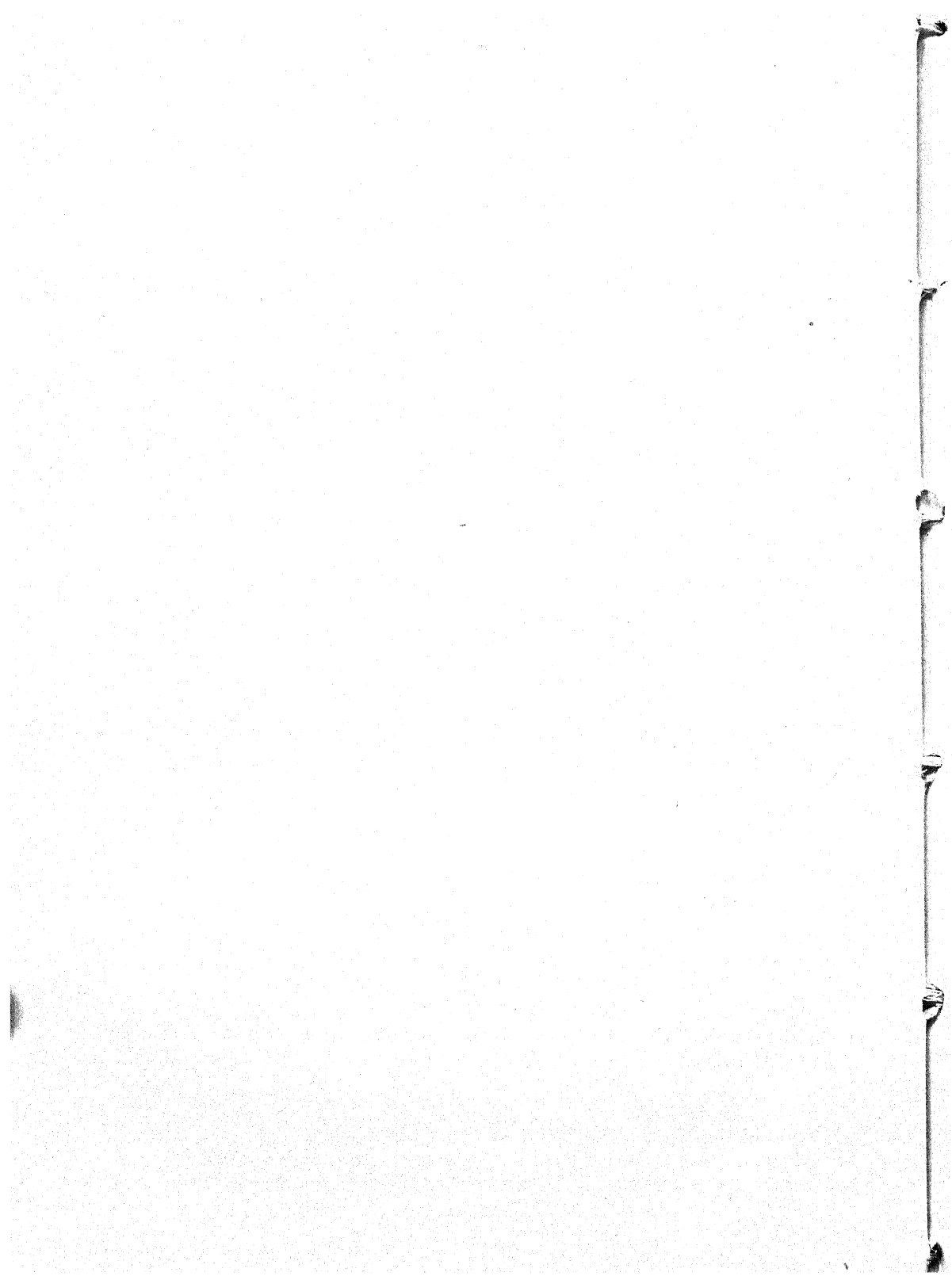
The storage of soils for 24 months at 10° or 20°C. produced a rather permanent change in their nitrifying microflora. In two out of the four soils stored at 40°C. the ability to produce nitrates had been lost.

Storage of soils at 10°, 20°, and 30°C. for 24 months had no significant effect upon their nitrogen-fixing powers, but storage at 40°C. materially reduced their nitrogen-fixing powers. When tested by the tumbler method, however, storage at 10°C. was found to reduce greatly the nitrogen-fixing powers of the soils as compared with similar soils stored at 20° or 30°C.

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SOME MODIFICATIONS IN THE NEUBAUER METHOD

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Experiment station chemists are confronted with unending requests for rather definite information on the nutrient requirements of the crops and soils of their states. A chemical analysis of a crop will tell the amount of nutrient elements removed from the soil, and an accurate determination of the total nutrient content of the soil can also be made. The value of such absolute data is limited, however, because of the multiplicity of factors associated with the performance of a crop on a particular soil. In attempts to measure this so-called availability of nutrient elements, many methods have been developed and are widely used. Among these, chemical methods are prominent. The chemical methods are admittedly empirical, and this is the substance of most objections to their use. In an attempt to overcome this objection, biological methods have been introduced, among which the Neubauer seedling test is important.

An empirical method may be defined as one in which the conditions of the test determine its quantitative value. The question arises then as to whether the biological tests, as applied to soils, may not be just as empirical as the chemical tests. The standard recommendation for the Neubauer test is 100 rye seeds and 100 gm. of soil, a 1:1 ratio, and a growing period of 15 days. Obviously the empiricism of the method, if such exists, should be determined by the magnitude of the values obtained by modifying certain steps in the technic of the method, particularly the number of plants, the weight of soil, and the kind of seedlings used. Experiments were therefore conducted involving modifications in procedure in which the number of seedlings was maintained at 100 and the weight of soil varied from 10 to 200 gm., in which the weight of the soil was maintained at 100 gm. and the number of seedlings varied from 25 to 200, in which the absolute weight of soil and the number of seedlings were varied from 10 to 100 but the ratio of weight of soil to number of seedlings was maintained at 1:1, and finally in which a number of other crop seedlings were grown instead of rye. The regular Neubauer procedure was followed except for the modifications mentioned, and regardless of weight of soil used the total weight of sand and soil was 350 gm. and the growing period 15 days.

The southwestern alkaline-calcareous soils used in these experiments have large reserves of phosphate, potassium, and calcium, for which the first has a low availability rating and the potassium and calcium have high availability ratings.

EFFECT OF VARIATION IN WEIGHT OF SOIL

In the first experiment eight soils were used, and the weight of soil varied from 10 to 200 gm. with 100 seedlings in each culture. Two series of cultures were grown, in duplicate, in one of which 30.2 mgm. of PO_4 was added. In these

fertilized soils the phosphate was added, in solution, to the soil, and the soil was allowed to dry in the air before being used in the cultures so as to simulate fixation. The Neubauer values obtained in this experiment are given in tables 1, 2, and 3 for phosphate (PO_4), potassium (K), and calcium (Ca).

TABLE 1

Variation in Neubauer PO_4 values with increase in weight of soil used in cultures

WEIGHT OF SOIL	PO_4 VALUES								Mean
	Soil No. 1	Soil No. 2	Soil No. 3	Soil No. 4	Soil No. 5	Soil No. 6	Soil No. 7	Soil No. 8	
gm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
<i>Unfertilized series</i>									
10	0.5	0.7	1.5	2.0	2.6	3.2	1.5	1.5	1.7
20	2.1	0.6	1.6	1.8	6.1	3.9	0.6	2.3	2.4
30	3.0	...	1.3	3.1	5.3	3.2	0.2	2.7	2.7
40	4.3	1.3	1.4	1.4	7.4	4.6	2.6	3.4	3.3
50	5.3	1.9	4.2	1.6	7.6	...	1.8	4.0	3.8
60	5.4	2.4	5.4	1.6	6.5	6.2	2.4	3.0	4.1
70	4.0	2.3	4.4	1.2	5.5	3.2	0.6	4.1	3.2
80	6.0	3.1	4.5	3.1	9.4	6.4	2.4	4.4	5.0
90	7.7	4.8	5.1	2.4	10.7	5.8	2.2	5.3	5.5
100	6.4	4.5	4.7	3.2	10.2	5.0	2.3	4.4	5.1
125	6.8	4.9	5.4	4.4	9.0	6.0	2.0	2.0	5.1
150	5.3	4.9	5.9	4.1	10.0	4.3	1.0	2.2	4.7
175	6.0	4.7	7.0	2.1	10.9	5.9	...	2.0	5.5
200	7.3	4.5	3.0	4.1	10.4	5.6	1.8	1.9	4.8
<i>Fertilized series</i>									
0	18.1	12.2	18.1	19.0	18.2	16.3	17.0
10	20.1	23.3	18.4	20.1	25.6	19.4	21.1
20	22.1	23.9	22.9	21.5	22.9	20.2	22.2
30	23.8	22.3	22.0	18.5	21.4	17.8	21.0
40	22.4	26.4	22.4	21.8	19.0	19.4	21.9
50	23.4	25.3	25.0	20.0	22.0	20.1	22.6
60	24.0	23.8	27.0	19.1	22.4	20.2	22.7
70	26.8	25.6	20.2	22.4	15.1	22.0
80	21.0	25.9	28.4	20.0	20.7	16.6	22.1
90	21.6	24.6	17.5	24.1	17.6	21.1
100	18.8	22.8	29.5	16.5	23.9	17.8	21.6
125	18.3	25.9	20.0	19.6	17.6	20.3
150	19.1	25.4	23.0	21.7	21.8	20.2	21.9
175	21.5	22.8	25.5	17.8	20.1	18.0	21.0
200	21.3	24.5	25.9	18.8	20.2	17.8	21.4

Phosphate. The absolute weight of soil which gave the highest Neubauer PO_4 value varied from 40 to 175 gm. Five of the soils attained the Thornton minimum value of 5.3 mgm. PO_4 , but only one attained the Neubauer-Schneider minimum value of 10.6 mgm. PO_4 even with 200 gm. of soil.¹ Of the five soils

¹ Thornton, S. F. 1935 Soil and fertilizer studies by the Neubauer method. Ind. Agr. Exp. Sta. Bul. 399.

that attained the Thornton minimum value, the absolute weight of soil at which this value was reached varied from 20 to 90 gm. The mean Neubauer values for the various weights of soil, given in the last column of table 1, show progressive increases in general, for the unfertilized soils, from 10 to 90 gm. of soil, beyond which there is no increase. This is true even for soils where the Neubauer values

TABLE 2
Variation in Neubauer K values with increase in weight of soil used in cultures

WEIGHT OF SOIL	K VALUES								
	Soil No. 1	Soil No. 2	Soil No. 3	Soil No. 4	Soil No. 5	Soil No. 6	Soil No. 7	Soil No. 8	Mean
gm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
<i>Unfertilized series</i>									
10	1.9	2.2	5.2	5.9	14.6	13.2	7.7	7.2
20	6.8	5.3	13.2	7.6	23.5	16.9	11.5	12.1
30	7.2	6.7	15.9	12.5	25.3	15.8	18.0	14.5
40	9.4	11.1	18.1	17.8	28.8	20.7	21.8	18.2
50	10.7	12.0	20.8	18.3	28.4	20.0	22.5	18.0	18.9
60	12.0	12.9	20.8	24.1	30.2	24.5	23.9	19.9	21.0
70	12.6	12.0	19.8	21.0	28.8	24.0	18.6	19.5
80	15.2	12.9	19.9	27.2	28.0	25.4	24.4	18.6	21.4
90	18.3	15.4	18.5	27.1	32.4	24.1	25.4	19.9	22.6
100	18.8	19.5	19.2	27.7	30.0	24.9	23.4	19.9	22.9
125	21.3	17.4	19.8	26.3	28.0	22.3	24.4	19.9	20.0
150	22.3	20.9	20.8	25.3	30.2	18.8	25.2	22.7	23.3
175	25.0	22.2	19.8	24.5	29.7	25.8	19.9	23.8
200	26.2	23.6	15.5	25.9	30.1	24.9	25.2	19.5	23.9
<i>Fertilized series</i>									
10	5.6	10.0	8.0	22.7	7.1	10.7
20	8.9	10.7	13.9	11.5	29.8	10.2	14.2
30	11.7	11.5	19.0	12.4	30.3	9.8	15.8
40	8.5	16.0	21.5	15.1	30.7	15.1	17.8
50	9.4	17.8	24.1	14.2	33.4	13.4	18.7
60	12.9	18.6	23.4	15.1	33.3	14.2	19.6
70	12.1	23.1	25.0	19.5	34.3	16.5	21.7
80	11.6	23.1	27.8	20.4	35.1	19.1	23.0
90	13.9	22.6	19.5	33.4	23.1	22.5
100	16.1	24.0	28.6	17.7	41.0	24.0	25.2
125	16.1	25.2	23.8	36.0	27.0	25.6
150	19.5	29.3	25.0	21.8	36.9	29.9	27.1
175	25.4	31.1	29.5	17.7	29.4	26.6
200	27.2	32.0	30.4	16.8	37.8	28.9	28.8

are very low and despite the fact that the amount of available phosphate present in the culture at 200 gm. is more than twice that at the point where the curve of mean values levels off. In the fertilized cultures the mean Neubauer values do not vary appreciably with weight of soil.

Potassium. The Neubauer K values are given in table 2. As with the PO_4

values, there is considerable variation in the absolute weight of soil which gives the highest K value. All the soils attained the Thornton minimum value of 8.3 mgm. K with 40 gm. of soil; with one exception, the Wheating² minimum K value of 11.6 mgm. K at 50 gm. of soil; and with three exceptions, the Neubauer-Schneider minimum value of 19.9 mgm. K at 100 gm. of soil. These results confirm the high availability rating that has been given to the semiarid soils of the southwest.

Calcium. The highest Neubauer Ca values also vary considerably with weight of soil. All these soils, except number 2, are calcareous. Negative Ca values are frequently obtained for alkaline-calcareous soils; that is, the seedlings from the soil cultures will often contain less calcium than the sand controls. In view of this, the values given in table 3 represent the total Ca per 100 plants and were not corrected for the sand controls. The mean Ca values indicate little or no additional uptake above 40 gm. of soil.

ADDITIONAL MODIFICATIONS IN WEIGHT OF SOIL AND NUMBER OF SEEDLINGS

In the next experiment only two soils were used, and both weight of soil and number of seedlings were varied according to the following outline:

<i>Number of seedlings</i>	<i>Grams of soil</i>
10	10
30	30
50	50
100	100
25	100
50	100
150	100
200	100

As in the previous experiment, the combined weight of sand and soil was 350 gm., and the seedlings were grown for 15 days. The values obtained from this experiment are given in table 4 as milligrams per number of plants grown in each culture and after calculation to a 100-plant basis.

On maintaining the ratio of number of seedlings to grams of soil at 1:1 but varying the absolute number of seedlings and the weight of soil from 10 to 100, there is naturally an increase in milligrams uptake with increase in weight and absolute number of seedlings. When these are calculated to a per plant basis, and correction is made for the sand control, Neubauer values decrease with increase in weight of soil and number of seedlings. A similar relation exists when the soil is maintained at 100 gm. and the number of seedlings is varied from 25 to 200. The milligrams uptake increases with increase in number of seedlings, but on a per plant basis the Neubauer values decrease with increase in number of seedlings.

² Wheating, L. C. 1930 A study of methods for the determination of the available potassium in soils. *Soil Sci.* 29: 1-21.

TABLE 3

Variation in Neubauer Ca values with increase in weight of soil used in cultures
Unfertilized series

WEIGHT OF SOIL	Ca VALUES								
	Soil No. 1	Soil No. 2	Soil No. 3	Soil No. 4	Soil No. 5	Soil No. 6	Soil No. 7	Soil No. 8	Mean
gm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
0	3.0	3.6	6.1	4.0	2.6	3.3	4.6	4.6	4.0
10	3.1	3.0	6.5	8.1	6.6	5.4	6.4	5.2	5.5
20	5.9	4.6	6.4	8.9	3.3	5.9	6.4	5.5	5.9
30	5.7	5.6	9.4	7.9	2.6	5.9	8.0	8.4	6.7
40	7.1	4.6	12.7	6.8	5.8	8.2	5.7	5.8	7.1
50	8.1	4.1	7.4	6.1	3.4	7.8	7.5	4.3	6.1
60	6.7	4.9	12.9	6.9	4.3	5.8	9.0	6.5	7.1
70	3.1	5.4	10.4	4.4	4.1	3.4	6.7	4.8	5.3
80	3.6	3.3	17.4	5.3	4.5	9.1	7.0	3.9	6.8
90	9.4	9.7	12.0	7.7	4.2	4.2	7.1	5.5	7.5
100	9.2	6.2	8.6	6.2	3.7	5.4	9.7	2.9	6.5
125	3.3	3.6	3.4	4.9	3.3	4.9	5.6	4.3	4.2
150	7.8	9.7	7.6	7.4	5.7	2.1	8.0	3.6	6.5
175	5.4	3.8	8.9	6.2	4.6	4.0	...	4.8	4.8
200	6.8	6.0	9.3	5.5	6.2	7.5	7.7	5.3	6.8

TABLE 4

Effect of variation in number of plants and weight of soil on Neubauer values*

WEIGHT OF SOIL—NUMBER OF PLANTS	K VALUES		PO ₄ VALUES		Ca VALUES PER 100 PLANTS
	Per culture	Per 100 plants	Per culture	Per 100 plants	
	mgm.	mgm.	mgm.	mgm.	mgm.

Soil No. 5

Sand	25.3*	28.3*	4.6*
10 gm. soil— 10 seedlings	7.5	75.0	4.2	42.0	19.0
30 — 30	17.3	57.7	10.8	36.0	10.0
50 — 50	26.6	53.2	18.9	37.8	6.8
100 —100	51.1	51.1	33.2	33.2	5.5
100 — 25	13.8	55.2	9.0	36.0	22.0
100 — 50	25.8	51.6	16.5	33.0	9.2
100 —150	61.3	40.8	46.3	30.8	2.7
100 —200	73.7	36.8	59.2	29.6	4.0

Soil No. 3

Sand	22.2*	27.4*	5.9*
10 gm. soil— 10 seedlings	9.8	98.0	5.1	51.0	16.0
30 — 30	17.6	58.8	10.3	34.3	12.4
50 — 50	26.4	52.8	20.6	41.2	18.0
100 —100	45.3	45.3	32.2	32.2	12.5
100 — 25	15.8	63.2	9.9	39.6	12.8
100 — 50	25.8	51.6	17.2	34.4	9.4
100 —150	65.3	43.6	46.7	31.2	9.2
100 —200	80.0	40.0	62.0	31.0	3.8

* Values for sand control are given but are not subtracted from values obtained with soils.

DISCUSSION OF DATA

Modifications in the Neubauer seedling test involving changes in absolute weight of soil but maintaining the number of seedlings constant at 100 yielded rather significant data. The mean PO_4 values in general increase steadily with increase in weight of soil up to 90 gm. and do not increase beyond this with increase in weight of soil. It is significant that all the PO_4 values for the eight soils used are low and that these values were not increased by increasing the weight of soil above 100 gm., despite the fact that the amount of available phosphate was thereby increased. Yet the PO_4 values were increased by adding a phosphate fertilizer to the soil. In Arizona soils, there are several major factors which influence uptake of PO_4 by plants. These are the physical condition of the soil, the calcium carbonate content, and the pH and degree to which the pH is buffered. By mixing or diluting the soil with silica sand the influence of all three of these is minimized; that is, aeration for the heavy soils is improved, the absolute weight of CaCO_3 is reduced, as is also the buffer capacity. These are all at a minimum when 10 gm. of soil is used, and increase with increase in weight of soil, and apparently above 100 gm. of soil these factors inhibit any further uptake of PO_4 unless phosphate fertilizer is added.

By reducing both the number of seedlings and the weight of soil and maintaining a 1:1 ratio, a greater relative uptake of PO_4 is attained by the lesser number of plants growing in smaller weights of soil, if the values are calculated to a per plant basis. Here again the dilution of factors inhibiting uptake is manifested. On further modifying the Neubauer test by increasing the number of seedlings above the recommended 100 per 100 gm. of soil, the magnitude of the value is also reduced as calculated to a 100-plant basis, but the absolute weight of PO_4 taken up from 100 gm. of soil increases with increase in number of seedlings. In other words, 100 plants are not able to take up any more PO_4 from 200 gm. of soil than from 100 gm., and by increasing the number of plants to 200 per 100 gm. a decreased amount of PO_4 per plant is taken up from the soil. The experiments show that the Neubauer values are greatly influenced by the absolute weight of soil and the number of seedlings, but that the 100/100 ratio which is standard for the method appears to be close to the point beyond which no further uptake occurs for alkaline-calcareous soils.

The K values also show a progressive increase with increase in weight of soil and number of seedlings, but unlike the PO_4 values, the mean K values and several K values of individual soils continue in a definite but small increase up to 200 gm. of soil. It appears that the selection of 100 gm. of soil and 100 seedlings is more arbitrary for potassium than for phosphate, especially in these soils, where there is a surplus of available potassium and the seedlings probably enjoy luxury consumption. It is significant that as the absolute weight of soil increases beyond 70 gm., at which weight the approximate Neubauer-Schneider minimum K value of 19.9 is attained, phosphate fertilization induces an additional uptake of potassium. Available phosphate is therefore a limiting factor in the uptake of potassium in these soils. When the method is modified to reduce the

number₁ of seedlings and the weight of soil, the per plant K values are highest for the smallest weights of soil and the least number of seedlings. On increasing the number of seedlings per 100 gm. of soil, above the recommended 100, the relative per plant uptake of K is also reduced.

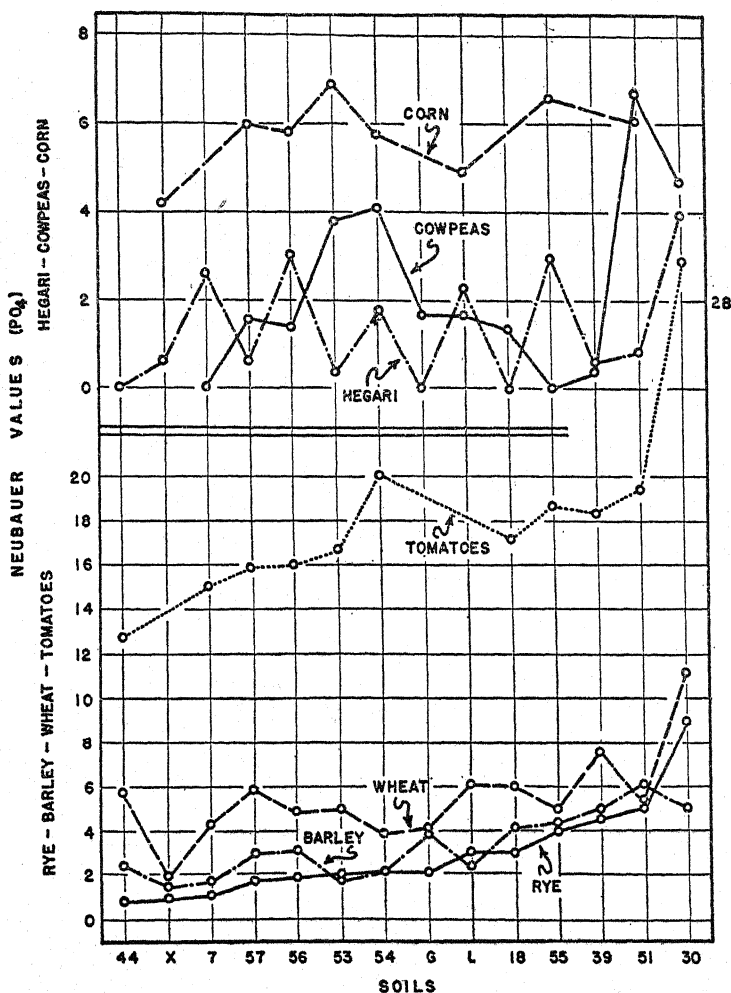


FIG. 1. COMPARISON OF NEUBAUER PO_4 VALUES FOR RYE, BARLEY, WHEAT, HEGARI, CORN, COWPEA, AND TOMATO SEEDLINGS

The calcium content of rye seedlings for a 15-day period of growth is very low as compared to potassium and phosphorus, and despite the calcareous nature of the soils the Ca values are low except for soil number 3, which contains 10.18 per cent $CaCO_3$ and is the highest in $CaCO_3$ of the soils used in the experiment. It is significant that at no weight of soil, when 100 seedlings are grown in the culture, do any of the other soils attain as high a Ca value as this soil, regardless of the

amount of CaCO_3 present. It is also significant that for soil number 3 the Ca values are lower in the range of 100–200 gm. of soil than in the range of 60–90 gm. When weight of soil and number of seedlings were maintained at a 1:1 ratio but below 100:100, a greater uptake of Ca per plant was obtained. Also, with 100 gm. of soil and varying numbers of seedlings, the greatest uptake of Ca, per plant, was obtained with the smallest number of plants.

COMPARISON OF RYE WITH OTHER SEEDLINGS

The Neubauer test has been criticised on the basis that no single plant can serve as an indicator of plant-food availability for all crops. The choice of seedlings suitable for such a test is limited to those of uniform seed and limited size of plants

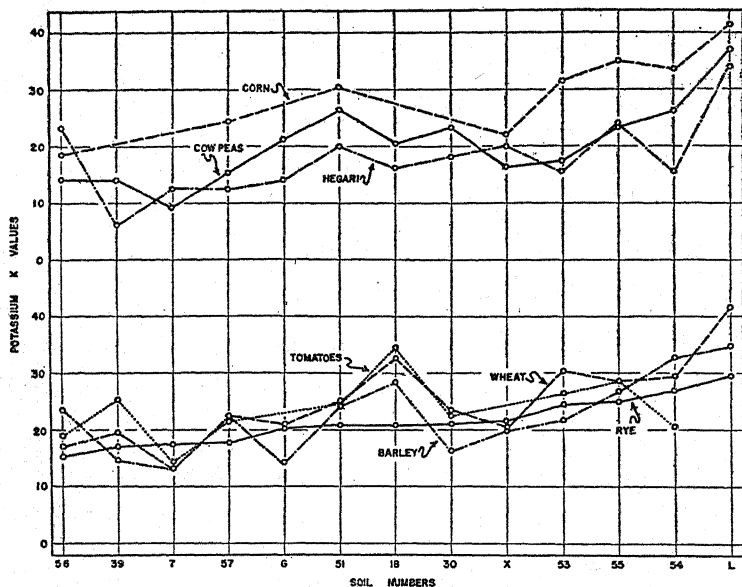


FIG. 2. COMPARISON OF NEUBAUER K VALUES FOR RYE, BARLEY, WHEAT, TOMATO, HEGARI, COWPEA, AND CORN SEEDLINGS

within a reasonable seedling period of growth. Rosen rye seems to fulfill these requirements quite satisfactorily and is suitable for both acid and alkaline soils. In view of the fact that Sacramento barley develops a more vigorous root growth than rye in alkaline-calcareous soils, an experiment was conducted in which a comparison was made between the Neubauer values obtained with these two grains. In this experiment 60 soils were used and a good agreement was obtained³. The uptake of both potassium and phosphorus, as measured by the mean values for the 60 soils, was higher for barley than for rye.

On the basis of this correlation, an experiment was conducted in which rye, wheat, barley, hegari, cowpeas, tomatoes, and corn were grown by the Neubauer

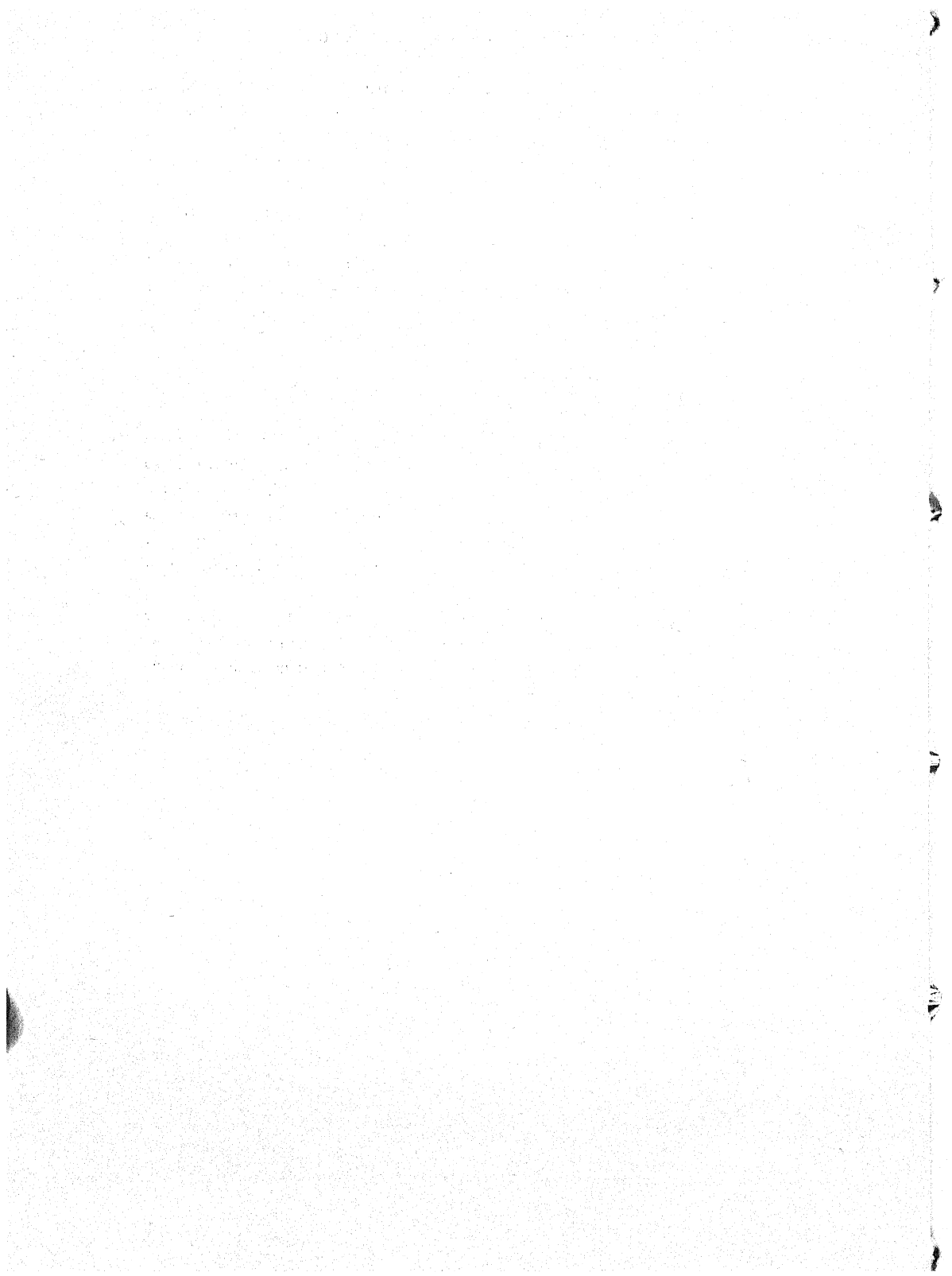
³ McGeorge, W. T. 1942 Studies in plant food availability in alkaline-calcareous soils: seedling tests and soil analysis. Ariz. Agr. Exp. Sta. Tech. Bul. 94.

technic. The PO_4 values obtained are given in figure 1 and the K values in figure 2. In all the cultures 100-gm. portions of soil were used and 100 seeds for rye, barley, wheat, hegari, and tomatoes, 50 seeds for cowpeas, and 25 seeds for corn. Correction for PO_4 and K for an equal number of seedlings grown in sand was made for all plants except tomatoes where no sand culture was grown. With due consideration of the fact that only ordinary seeds were obtainable for all except rye, the following conclusions appear warranted. Correlation of PO_4 values is good for rye, wheat, barley, and tomatoes and is fair for corn. The K values show a good correlation for all seven crops. There is evidence, then, that though different seedlings extract different amounts of the nutrient elements from the soil because of a difference in feeding power and requirements, the directional trend of the curves is in good agreement.

SUMMARY AND CONCLUSIONS

In a study made to determine the effect of certain modifications of procedure on the Neubauer seedling test, it is shown that both the ratio and the absolute weight and number of seedlings must be maintained at 100:100, but in availability studies informative data can be obtained by modifying the procedure to use lower weights of soil. The Neubauer test, like the chemical analysis of a soil, is an empirical test because the conditions must be closely adhered to in order to obtain quantitative values.

When the Neubauer test is modified by comparing uptake of nutrient elements by rye and other seedlings the data are confused by lack of uniformity of seed. There is, however, strong evidence that the availability measured with rye seedlings is applicable to many other crops.



THE INFLUENCE OF HIGH CONCENTRATIONS OF SODIUM SULFATE, SODIUM CHLORIDE, CALCIUM CHLORIDE, AND MAGNESIUM CHLORIDE ON THE GROWTH OF GUAYULE IN SAND CULTURE

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During 1942 and 1943, the acreage of guayule in the Southwest was greatly increased through the efforts of the Emergency Rubber Project. Because of the prevalence of salinity in the irrigable soils of these southwestern states, it was inevitable that some of these plantings would be made on land more or less saline. Virtually nothing was known of the tolerance of the guayule plant to the various salts found in saline soils. It seemed advisable, therefore, to gain some information on the relative salt tolerance of the plant.

Three separate experiments pertaining to the salt tolerance of guayule were carried out in sand culture. The results of all three experiments were similar, and therefore only the final experiment is reported in this paper.

The plants used in the study were obtained from the Alisal Nursery of the Emergency Rubber Project. As received, the plants had taproots 20 to 25 cm. long and 3 to 5 mm. in diameter at the crown, and the tops had been trimmed to 5 to 8 cm. in height. They were first imbedded in sand and allowed to initiate a new flush of growth before selection of plants for study. On March 15, 1943, after the plants had been in the sand bed for about 6 weeks, 39 uniform plants were selected out of the original hundred and each was transplanted to a 5-gallon crock of sand. Each culture was part of an automatically flushed sand culture apparatus which included a reservoir of 20 liters of culture solution for each culture (1). Differential treatment was initiated 2 weeks after the plants were transplanted to the sand cultures.

The basal nutrient solution employed contained the following ion concentration when made up with Riverside tap water:

ion	m.e./l.	ion	m.e./l.
Ca.....	5.9	Cl.....	2.7
Mg.....	2.7	SO ₄	4.3
Na.....	1.5	H ₂ PO ₄	0.75
K.....	2.5	NO ₃	5.0

Iron, manganese, and boron were also supplied at the rate of 0.5 p.p.m. This solution had an osmotic pressure of 0.45 atmosphere. It was used as one of the 13 cultural treatments. The other 12 treatments consisted of adding a given salt to the basal solution to increase its osmotic pressure by 1, 2, and 3 atmos-

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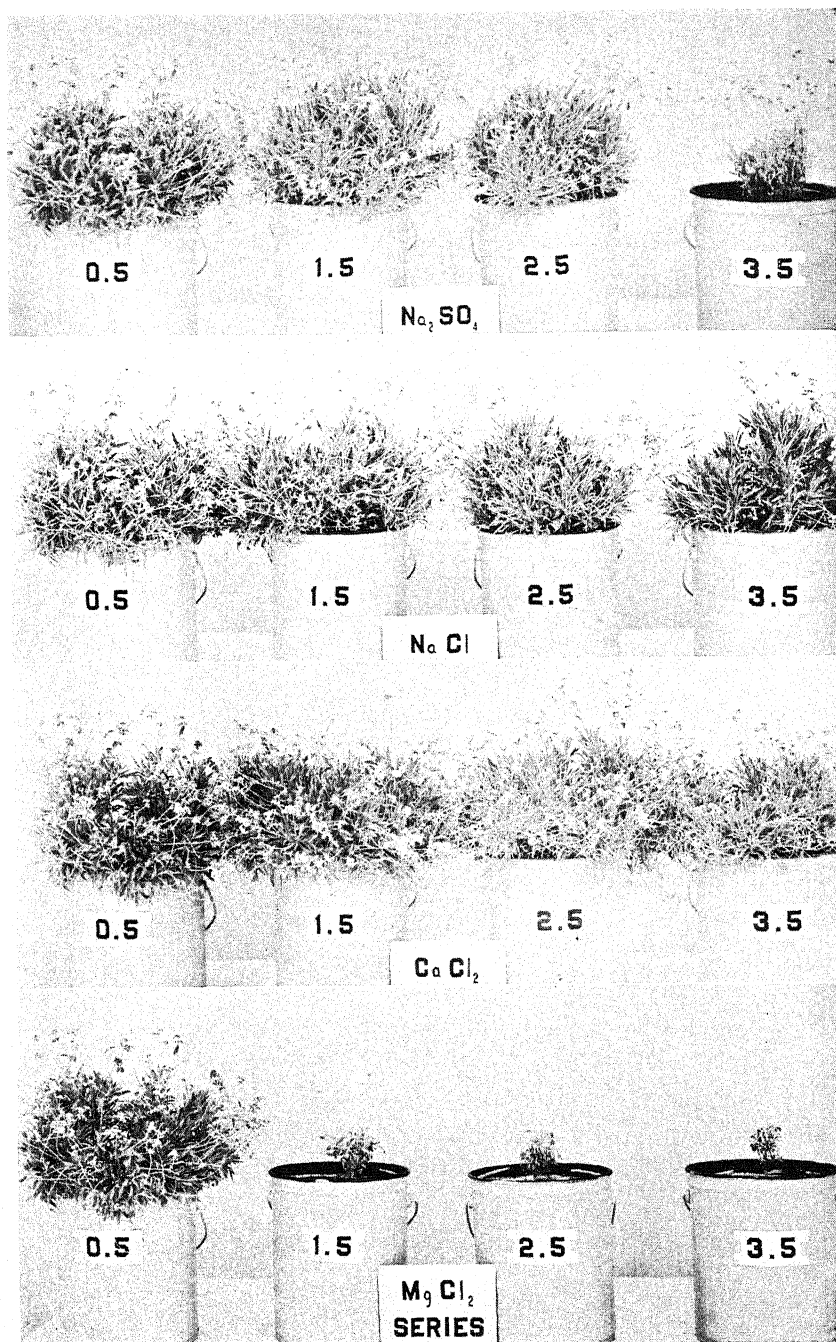


FIG. 1. APPEARANCE OF GUAYULE PLANTS AT TERMINATION OF EXPERIMENT
Numbers on containers designate osmotic pressures of culture solutions in atmospheres. That at 0.5 atmosphere is the basal nutrient. Higher concentrations attained by adding necessary amounts of designated salts.

pheres. Na_2SO_4 , NaCl , CaCl_2 , and MgCl_2 were the salts studied. Each treatment was thrice replicated. The 20 liters of culture solution contained in the reservoir (1) of each culture was changed weekly. Between changes, the volume and the concentration of the culture solution were maintained by additions of distilled water.

Figure 1 shows the appearance of the plants as of July 13, 1943, the date the experiment was terminated. Figure 2 shows the effect of salt treatment on average dry weight per plant.

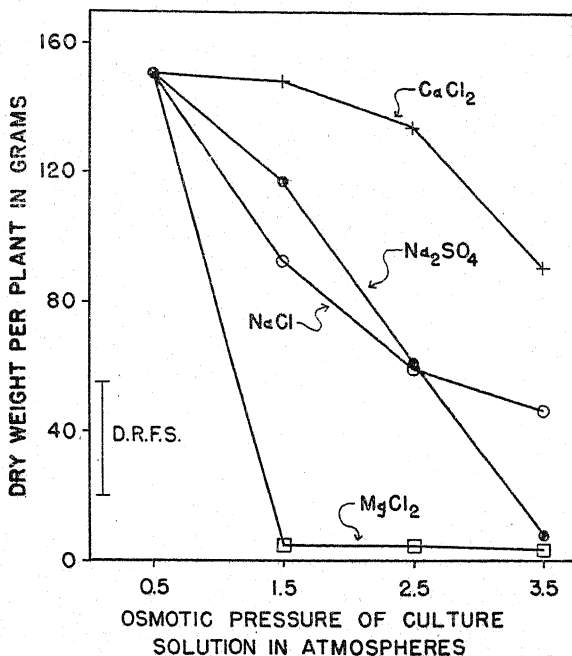


FIG. 2. AVERAGE DRY WEIGHTS OF TOPS OF PLANTS GROWN UNDER THE VARIOUS TREATMENTS

D.R.F.S. designates difference required for significance. Observations on the MgCl_2 cultures were omitted from the estimation of pooled error, since they were not homogeneous with the rest of the observations.

The most striking observation made with respect to these plants was their sensitivity to magnesium. For example, red kidney beans showed only about a 10 per cent reduction in growth when 1 atmosphere of MgCl_2 was added to the control nutrient solution (2), whereas guayule was killed by this concentration of MgCl_2 in the substrate. One week after treatment was initiated, the plants supplied with 3 atmospheres of added MgCl_2 were showing magnesium-toxicity symptoms. The young leaves failed to expand normally, their tips became necrotic, and they were light yellow green. Three weeks after treatment was initiated, all plants supplied with added MgCl_2 were showing magnesium-toxicity symptoms. All of these plants died before the end of the experimental period.

An examination of their roots at the termination of the experiment indicated that very little root growth was made by any of these plants after initiation of treatment.

By contrast, guayule was remarkably tolerant of CaCl_2 . This tolerance to calcium may be related to the fact that the species is indigenous to calcareous soils (3).

Guayule is rather sensitive to sodium salts. At the lower concentrations studied, isosmotic pressures of NaCl and Na_2SO_4 had nearly the same effect on growth. When 3 or more atmospheres of salt was added, Na_2SO_4 had a distinct toxic effect. In fact, some of the plants died when 3 atmospheres of Na_2SO_4 was added, whereas guayule will make some growth in the presence of 5 atmospheres of added NaCl .

This study indicates that, by and large, guayule may not be regarded as a salt-tolerant plant. Furthermore, the plant shows considerable specificity toward the kind of ions present in excess, whereas many crop plants show little specificity in growth response to kind of salt, osmotic pressure of the solution being the predominant factor in determining growth (4).

There has been some tendency to evaluate degree of salinity of a soil in terms of the amount of chloride ion present, on the assumption that the effect of soil salinity on plant response was largely that of chloride toxicity. On the basis of the present observations this might be a dubious procedure with reference to guayule. This plant tolerated rather high concentrations of calcium chloride, but was very sensitive to rather low concentrations of magnesium chloride. This suggests that concentration of the chloride ion *per se* would be a poor indicator of the inhibitive effect of a given substrate on growth unless information was available as to the cationic composition of the solutes present.

No rubber determinations were made on these plants. The plants grown in an earlier study on the effect of salt concentration on growth of guayule were harvested at a similar stage of growth as those here reported, however, and were assayed for rubber by the Emergency Rubber Project. Only 0.2 to 0.6 per cent rubber was found in the plants, with more variation in evidence between replicates than between treatments. These results suggested the futility of making rubber analyses on plants at the age and growth status of those employed in this study.

SUMMARY

Guayule plants were grown in sand culture with a control nutrient solution, and in cultures with this same solution but with 1, 2, and 3 atmospheres osmotic pressure of an added salt. Four salts were studied separately, viz., Na_2SO_4 , NaCl , CaCl_2 , and MgCl_2 .

This species is very sensitive to magnesium, the plants being killed by the lowest concentration of MgCl_2 used.

Guayule is very tolerant of CaCl_2 , making fairly satisfactory growth in the presence of 3 atmospheres osmotic pressure of added CaCl_2 .

The plants were relatively sensitive to sodium salts, and at the higher concentrations they were more sensitive to Na_2SO_4 than to NaCl at isosmotic pressures.

In the light of these studies guayule may not be regarded as a salt-tolerant plant.

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CHANGES IN pH AND IN BASE-EXCHANGE PROPERTIES OF CRANBERRY SOILS FOLLOWING THE USE OF ALKALINE WATER

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The greenhouse experiments here reported were undertaken to determine the extent to which the pH and base-exchange properties of cranberry soil may be altered by the continued use of alkaline water. Although the conditions under which the experiments were carried out are different from those existing in cranberry culture, it is hard to escape the conclusion that changes resembling those here observed might eventually occur under cranberry culture if alkaline flooding water is regularly used.

USE OF WATER IN CRANBERRY CULTURE

Water for flooding has long been a prime necessity in cranberry culture. The plants are flooded to prevent frost damage and winter injury, to control insects, and, in Wisconsin, also to facilitate harvesting. So important is water in cranberry culture that in 1929 Wood County, Wisconsin, had about 7 acres of reservoir for each acre of vines. Although the water used for flooding on a majority of Wisconsin cranberry marshes is between pH 6 and 7, in a number of cases the water is between pH 7 and 7.5, and in a few it is above pH 8.

A possible relation between the use of alkaline flooding water and certain problems in cranberry growing was first mentioned in print in 1940 by Stevens, Rogers, and Bain.¹ Based on 15 years of field work and a study of the history of the cranberry industry in Wisconsin, the conclusions of these workers were as follows:

The use of alkaline water in flooding cranberry marshes greatly increases the difficulties of producing profitable crops of berries.

The difficulties tend to become greater as the alkalinity of the water becomes higher.

The effects are, to a certain degree, cumulative, being more evident and more serious in older marshes after alkaline water has been used for a number of years.

The foregoing observations suggest the possibility that continued flooding with alkaline water has so changed the character of certain soils as to make them much less favorable for cranberry growing. There is considerable evidence that repeated irrigation of certain soils in rice culture has a tendency to reduce their acidity, in some cases rendering them alkaline. The literature on this subject was reviewed by Reed and Sturgis² in 1939.

¹ Stevens, N. E., Rogers, L. M., and Bain, H. F. 1940 Alkaline flooding water in cranberry growing. *Trans. Wis. Acad. Sci., Arts, and Letters* 32: 351-360.

² Reed, F. J., and Sturgis, M. B. 1939 Chemical characteristics of the soils of the rice area of Louisiana. *La. State Univ. Bul.* 307.

This paper is not directly concerned with the question of the most favorable soil conditions for cranberry culture, but with the specific problem as to whether repeated flooding with alkaline water would materially change the reaction of the Wisconsin cranberry soils.

The results of the tests may also have some direct interest in connection with the effects of hard water on greenhouse soils. Spurway and Wildon³ have devised a method using phosphoric acid for eliminating the alkalinity of hard water used in greenhouse culture.

EXPERIMENTAL METHODS

Six samples of soil (peat) were used in the experiment. Three, Durphee (Sawyer County), Morrison (Jackson County), and Williams (near Biron,

TABLE 1

Changes in pH, in content of exchangeable calcium and magnesium, in base-exchange capacity, and in percentage base saturation of peat caused by additions of alkaline water over a 2-year period under greenhouse conditions

LOCATION OF PEAT	pH (GLASS ELECTRODE METHOD)			EXCHANGEABLE CALCIUM			EXCHANGEABLE MAGNESIUM			TOTAL EXCHANGE- ABLE CALCIUM AND MAG- NESIUM		BASE-EX- CHANGE CAPACITY		PERCENTAGE BASE SATURATION	
	At beginning	After 1 year	After 2 years	At beginning	After 1 year	After 2 years	At beginning	After 1 year	After 2 years	At beginning	After 2 years	At beginning	After 2 years	At beginning	After 2 years
				m.e.*	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.		
Valley Jct.	4.22	4.20	5.33	5.56	17.40	2.14	11.00	7.70	28.40	49.0	76.4	15.7	37.2
Morrison	4.01	4.25	5.30	2.44	5.60	9.00	1.60	3.76	5.80	4.04	14.80	47.0	56.6	8.6	24.4
Durphee	3.60	3.98	5.00	7.14	12.56	26.80	3.21	6.95	16.80	10.35	43.60	99.3	113.1	10.4	38.6
Bennett	4.70	4.60	5.77	12.65	37.10	3.56	19.50	16.21	56.60	57.0	120.5	28.4	47.0
Cutler	5.01	4.90	6.40	21.40	39.40	5.35	14.40	26.75	53.80	34.9	58.2	76.6	92.5
Williams	4.38	4.30	5.60	11.30	28.90	3.06	11.30	14.36	40.20	45.0	69.4	32.0	57.9

* In this table, m.e. = m.e. per 100 gm. soil.

Wood County), were taken from cranberry fields. The sample designated "Cutler" was taken from a field in Juneau County which was under construction, but the land had been in cranberries prior to 1893. The sample designated "Valley Junction" (Monroe County) was taken from a marsh that has been in cranberries for at least 60 years, and the Bennett (Cranmoore—Wood County) marsh has been in cranberries for at least 70 years.

Two 2-gallon earthenware jars were filled with soil from each sample, and cranberry vines were planted in the jars, which were then placed (September, 1941) in a greenhouse. For 1 year they were irrigated with water from Lake Mendota, which has a pH of 7.8 to 8.4, an alkalinity expressed as calcium

³ Spurway, C. H., and Wildon, C. E. 1938 Water conditioning for greenhouses. *Mich. Agr. Exp. Sta. Cir. Bul.* 166.

carbonate of 160 to 170 p.p.m., a hardness of 180, and a mineral content of 202 p.p.m.

In September, 1942, they were moved to Urbana, Illinois, and irrigated for the next year with water having a pH of 7.4 to 7.6, an alkalinity expressed as calcium carbonate of 325 to 350 p.p.m., a hardness of 250 to 275, and a mineral content of 350 to 360 p.p.m.

Before the addition of alkaline water to these soils, determinations were made for pH, exchangeable calcium and magnesium, and base-exchange capacity. After 1 year's treatment, pH readings were made, and the exchangeable calcium and magnesium determined on those soils which showed a rise in pH value. After 2 years' irrigation, the pH, exchangeable calcium and magnesium, and the base-exchange capacity were again determined.

RESULTS

The results of the analyses are given in table 1. It will be observed that there were decided increases not only in pH values and amounts of exchangeable calcium and magnesium present, but also in the base-exchange capacity.

An increase in pH value was not detected after 1 year's treatment, except on the Morrison and Durphee samples. The former increased from pH 4.01 to 4.25, and the latter from pH 3.60 to 3.98. Since an increase in pH value of 0.3 reduces the intensity of acidity by one half, the use of alkaline water on these soils had a marked effect in 1 year's time.

At the end of 2 years' treatment with alkaline water, the pH values increased from 1 unit in the Bennett peat to 1.4 in the Durphee soil. As a difference in pH value of 1 unit makes a difference of ten times in the strength of the acidity (in the acid range), these soils were only one-tenth as acid as they were 2 years previously, that is, before treatment with alkaline water.

Since the amounts of exchangeable sodium and potassium present were insignificant in comparison to the calcium and magnesium, they were ignored in these calculations.

At the end of 2 years' treatment, the amounts of exchangeable calcium and exchangeable magnesium had increased markedly in all samples. These bases had, of course, been absorbed from the alkaline water used in treating the soils.

The increase in base-exchange capacity probably resulted from a transformation of certain types or organic material to new forms which had more pronounced base-exchange properties; this transformation was undoubtedly hastened by the higher temperatures of the greenhouse compared to those in the field. The higher pH values may also have favored this transformation. Even though the base-exchange capacity increased, sufficient bases were absorbed to cause a considerable rise in the percentage base saturation and in the pH value.

CONCLUSIONS

It appears that repeated flooding of cranberry soils with alkaline water will increase the base saturation to such an extent that an undesirably high pH

value may result. Although under greenhouse conditions this can be brought about in a few years, it will probably take much longer in field practice. Since cranberry marshes are maintained for a long time, it appears probable that the practice of regularly using alkaline water for flooding purposes will eventually raise the pH to such an extent that the marshes may cease to be profitable for cranberry culture.

BOOKS

Colloid Chemistry. Collected and edited by JEROME ALEXANDER. Reinhold Publishing Corporation, New York, 1944. Pp. 1256. Price, \$20.

This is the fifth volume of the "Theory and Methods, Biology and Medicine" series. It contains 60 papers prepared by a "distinguished group of contributors who represent a variety of natural origins." Among the topics considered are: surfaces of solids and liquids, soaps and detergents, analysis of complex molecular structure, microradiography, electron microscope, rheological properties of colloidal materials, high-vacuum distillation, polymerization, vitreous state, sonic and ultrasonic waves, cyclotron, betatron, electrophoretic studies of proteins, high-speed centrifugation, selective adsorption, fixing dates of past events by tree rings and varves, proteins, photosynthesis, plant cell membranes, starches, enzymes, minerals and vitamins, hormones, physiological rhythms, viruses, genes, protoplasm, inflammation, blood coagulation, immunology, allergy, homeostasis, cancer, gerontology, concretions, war gases, infective aerosols, lipides, psychiatry, and changes in surrounding medium produced by free-living cells. Any scientist, no matter what the field of endeavor, will find much material of great interest and value in this volume. Certainly every library should contain a copy of this book, and every research worker who can afford to own it will want a copy for his personal use.

The Green Continent. Selected and edited by GERMAN ARCINIEGAS. Alfred A. Knopf, New York, 1944. Pp. 533. Price, \$3.50.

Those who contemplate studying the agriculture or the industry of Latin America, whether by reading or travel, would do well to read this book, which gives a comprehensive view of the countries to the south of us as seen by their leading writers. Its 33 articles are not merely good literature but they are highly informative about the cities, the mountains, and the plains, and the people who dwell therein. All of the material was prepared originally for domestic consumption and is, therefore, quite critical, containing nothing that might be classed as propaganda. The book is worth the price for entertaining reading, but it has double value for those whose interest in Latin America is more specific. Its one weakness is that it does not contain a good map of Central and South America.

Soil Science Society of America Proceedings. Volume 8. The Soil Science Society of America, G. G. Pohlman, Sec.-Treas., Morgantown, West Virginia, 1944. Pp. 473. Price, \$5.

This volume contains the papers presented at the meetings of the Society that were held in Cincinnati, Ohio, November 10-12, 1943. The general program consisted of seven papers commemorating the 100th anniversary of the founding of the Rothamsted Experimental Station, four papers on the efficient use of fertilizers during the war, and a banquet-program paper presented by Howard M.

Call, a prominent farmer from Kent, Ohio, on "The Old Home Farm—One Hundred and Forty Years Ago to Now." The special programs, built around the Society's six sections, physics, chemistry, microbiology, fertility, genesis (including morphology and cartography), and technology of soils, consisted of 83 papers prepared by specialists in these fields of study. The minutes of the business meetings, a list of the officers for 1944, and the membership of the standing committees are appended. The variety and quality of the papers contained in the Proceedings make it imperative that every soil scientist have a copy available for ready reference.

The Soils of Equatorial Regions. By E. C. JUL. MOHR. Translated by Robert L. Pendleton. Edwards Brothers, Inc., Ann Arbor, Michigan, 1944. Pp. 766, figs. 257. Price, \$7.50.

Dr. Pendleton is to be highly commended for his enterprise in translating from the Dutch language this very valuable contribution on the climate, soil, and agriculture of the Netherlands East Indies. The lithoprinting is well done, and the illustrations are excellent reproductions of drawings and tropical scenes. The book is certain to be widely read by a great variety of people who will approach the subject from diverse points of view. It would be very helpful if someone would prepare a digest of this volume, picking out the unique comments that occur from page to page. Thus, in speaking of various portions of the several islands making up the East Indies, the author writes: "... the continuous humid climate of these regions does not promote permanent conservation of fertility ... the hydrogen clay is perhaps less than 5 per cent saturated with bases, as contrasted with being more than 95 per cent saturated with hydrogen ... the humus coming from a certain plant or plants may not, by a great deal, be the same as the humus from another sort of plant [referring to the minor elements] ... for the production of tobacco on some lands, a very long fallow, for 25 or 50 years at least, is necessary ... the more acid and poorer in iron the original rock was, and the greater the degree of senility of the soil, the greater the chance of failure under cultivation." This book provides an excellent illustration of the contribution a scientist with curiosity and tenacity of purpose can make to his chosen field of endeavor in the course of a lifetime.

THE EDITORS.

IRON OXIDE REMOVAL FROM CLAYS AND ITS INFLUENCE ON BASE-EXCHANGE PROPERTIES AND X-RAY DIFFRACTION PATTERNS OF THE CLAYS¹

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Recent investigations concerned with the identification and characterization of soil clays have led to a special interest in the problem of the removal of the free iron oxides from these clays without serious alteration of the clay minerals proper. The methods thus far proposed for this purpose have proved to be unduly destructive of those clays containing iron in their crystal lattice, or have other objectionable features. It was for the purpose of developing a method which would overcome some or all of these objectionable features that the present study was undertaken. The influence of iron oxide removal on base exchange properties and x-ray diffraction patterns of the clays was also investigated.

REVIEW OF LITERATURE

Various methods have been suggested for the removal and estimation of the free iron oxides of soils. Tamm (18) used acid ammonium oxalate to dissolve iron oxides, free silica, and alumina. Lundblad (13), using Tamm's extracting solution on Sharkey, Sassafras, and Nipe soils and on a New Zealand soil, found a higher base-exchange capacity after extraction than before, calculated on original sample weight. Drosdoff (8) used a 0.2 *N* sodium acid oxalate extracting solution and reported increases in base-exchange capacity after treatment. From 5 to 20 per cent of material other than free iron oxides was dissolved.

Drosdoff and Truog (7) made the ferric oxides more soluble by H_2S reduction. The suspension was saturated with H_2S , made alkaline with NH_4OH , and the clay washed with 0.05 *N* HCl to dissolve the iron sulfides. The treatment readily dissolved finely ground iron oxides but had no appreciable effect on the iron in biotite, basalt, and granite. Free iron oxides were removed from two soil colloids and a bentonite with no significant change in the base-exchange capacity. Toth (19) used this H_2S treatment and reported small increases in base-exchange capacities of clays from Colts Neck and Sharkey soils, but appreciable decreases in others. Drosdoff (9) more recently proposed saturation of an ammoniacal clay suspension with hydrogen sulfide, and subsequent solution of the sulfides with hydrogen peroxide and excess sulfuric acid.

In a procedure proposed by Truog *et al.* (20) nascent H_2S is evolved within the clay suspension by the action of oxalic acid on Na_2S . Oxalic acid is preferred to mineral acid because of its more efficient solvent action on iron oxides. The stability of aluminum exchange material and the susceptibility of iron exchange material to this treatment were demonstrated. Increase in base-exchange capacity as the result of the treatment was noted with Cecil soil.

¹ Part of a thesis submitted in partial fulfillment of the requirements for the degree of doctor of philosophy, department of soils, University of Wisconsin. This work was supported in part by a grant from the Wisconsin Alumni Research Foundation. Published with the permission of the director of the Wisconsin Agricultural Experiment Station. Appreciation is expressed to E. Truog and M. L. Jackson for helpful suggestions and criticisms and for aid with the x-ray diffraction analyses.

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Alexander and Hendricks (2) and Alexander *et al.* (3) established by x-ray diffraction methods the presence of goethite and hematite in the untreated clay of Cecil, Greenville, Decatur, Dewey, Chester, Manor, and Hagerstown soils, goethite alone in clay from Fullerton and Frederick soils, and their absence in the clays treated by the Na_2S -oxalic acid method. Crystalline iron oxides were not detected in the clays of Miami, Carrington, Barnes, or a desert soil, although up to 10 per cent Fe_2O_3 was extracted. The total loss in weight as a result of the treatment was 10 to 40 per cent. Nagelschmidt (16) found goethite and hematite in the C horizon of Cecil soil by x-ray diffraction methods, and reported that the Na_2S -oxalic acid treatment completely removed these oxides; 20 per cent of a Barnes B_2 colloid and 10 to 15 per cent of a bentonite colloid were dissolved.

Jeffries (12) used nascent hydrogen produced by the action of oxalic acid on a cylinder of aluminum immersed in the boiling soil suspension to reduce the free iron oxides. Clean silt and sand fractions were obtained for petrographic analysis, and preliminary studies indicated that the treatment was not destructive to clay minerals.

Allison and Scarseth (4) employed anaerobic fermentation for reduction of free iron oxides in soil colloids. The free iron oxides were reduced and dissolved as a result of a lowered oxidation-reduction potential and the production of organic acids in the fermentation. The results indicated similarity to the Na_2S -oxalic acid method. Treatment of clay from a Miami soil from Indiana by either method resulted in large increases in base-exchange capacity.

REMOVAL OF IRON OXIDES FROM CLAYS WITH DIFFERENT METHODS

In the preliminary investigations it was observed that the decrease in base-exchange capacity as a result of the Na_2S -oxalic acid treatment could be greatly reduced by the substitution of tartaric acid for oxalic acid, and by avoiding greater acidity than that required just to dissolve the ferrous sulfides.

Comparison of oxalic and tartaric acids

To compare the destructiveness of oxalic and tartaric acids on iron-bearing base-exchange minerals, a series of 0.335-gm. samples of the Miami clay fraction³ were digested for 4 days on the steam plate in 500-ml. portions of 0.2 *N* ammonium oxalate solution of pH 5 and ammonium tartrate solutions of pH 4.5, 5.0, and 6.0. The pH adjustments were made by adding HCl. This clay owes approximately half of its base-exchange capacity to iron-bearing base-exchange material, according to Simonson.⁴ The samples were recovered by centrifuging and were washed three times with *N* NH_4Ac acidified with HCl to remove the dissolved iron. Iron was determined in the decantate by the cupferron method (17), and the base-exchange capacity, by the manganese method (5).

The results (table 1) show that ammonium oxalate was more destructive of base-exchange material than ammonium tartrate, and that destruction with the tartrate increased progressively with increasing acidity. At pH 6.0 ammonium tartrate still removed an appreciable amount of iron, and caused an increase rather than a decrease in base-exchange capacity.

³ In this paper "clay fraction" refers to particles less than 2μ in diameter, unless otherwise specified.

⁴ Simonson, R. W. Base-exchange capacity of soils due to iron compounds. 1938. [Unpublished doctoral thesis. Copy on file, Dept. of Soils, Univ. Wis., Madison.]

Proposed aluminum-ammonium tartrate method

The proposed procedure employing nascent hydrogen for the reduction and solution of free iron oxides from soils utilizes ammonium tartrate instead of oxalic acid (12) to produce the nascent hydrogen by action with metallic aluminum. Ammonia is released by the combination of aluminum and the tartrate ions and removed by boiling, giving the solution a constant pH of 6.4, which is less destructive to the clay than more acid solutions. The clay in suspension is brought into intimate contact with the source of nascent hydrogen during the digestion by the introduction of a closely wound aluminum spiral (0.04- by 2.2-cm. ribbon) into the suspension and by employing an aluminum vessel (16-ounce measuring cup) as a container.

Details of procedure. To the aluminum vessel containing the spiral, a 10-gm. sample of soil (previously treated with hydrogen peroxide to remove organic matter) or a 0.5- to 1.0-gm. sample of clay is added, followed by 100 ml. of distilled water containing 10 gm. of ammonium tartrate. The suspension is main-

TABLE 1

Effect of digestion of clay from Miami silt loam (B₂ horizon) with acid oxalate and tartrate solutions on the base-exchange capacity

DIGESTING SOLUTION	BASE-EXCHANGE CAPACITY BASED ON ORIGINAL WEIGHT	Fe ₂ O ₃ REMOVED	COLOR OF CLAY SUSPENSION
	<i>m.e./100 gm.</i>	<i>per cent</i>	
None (check).....	58.0	Brownish
Ammonium oxalate of pH 5.0.....	23.2	9.08	Grayish white
Ammonium tartrate of pH 4.5.....	40.1	6.86	Yellowish white
Ammonium tartrate of pH 5.0.....	52.3	4.03	Yellow-brown
Ammonium tartrate of pH 6.0.....	62.8	3.46	Yellow-brown

tained at slow boiling until solution of the iron oxides has proceeded to the point desired, as indicated by the absence of the red or yellow color of free iron oxides in the suspension. This usually takes 10 to 45 minutes.

When digestion is complete, the suspension is poured into a beaker, and the cup and spiral are washed three times with small amounts of *N* NH₄Ac, and finally once with 0.05 NHCl. By means of the centrifuge procedure, the sample is recovered from suspension and washed three times with *N* NaCl (acidified to pH 3.0). The decantate and washings are combined and saved for the determination of dissolved constituents.

To remove colloidal silica and to facilitate flocculation of the clay, the sample is digested for 30 minutes in boiling 2 per cent Na₂CO₃ solution, preferably in a nickel dish, and recovered by centrifuging. It is then washed twice with *N* NaCl, twice with *N* NaAc of pH 3.5 (acidified with HCl), four times with 0.5 *N* Ca(Ac)₂ of pH 7.7, and finally twice with *N* NH₄Ac of pH 7.0 so as to free the material of carbonates and exchangeable hydrogen. Use of these preliminary washings preceded all exchange-capacity determinations herein reported.

If iron alone is to be determined in the ammonium tartrate solution, it is precipitated with cupferron and determined volumetrically. If both aluminum and iron are to be determined by precipitation as the hydroxides, the tartrate is first destroyed by several treatments with aqua regia, since the tartrate interferes with the precipitation of iron and aluminum as the hydroxides. Aluminum dissolved from the clay or soil is calculated by subtracting from the total aluminum found in solution the loss in weight by the cup and spiral during digestion.

It was found that long digestion in the tartrate solution (more than 2 hours), unless followed by digestion with Na_2CO_3 , led to difficulties in flocculation and recovery of the clays by centrifuging. After this alkaline digestion, the clays flocculate normally, and this treatment is probably desirable even after shorter tartrate digestions.

TABLE 2

Effect of aluminum-ammonium tartrate treatment of various clay minerals on their base-exchange capacities and on solution of constituents

MINERAL TREATED	TREATMENT	BASE-EXCHANGE CAPACITIES BASED ON ORIGINAL WEIGHT	EXTENT OF SOLUTION		TOTAL Fe_2O_3 CONTENT OF CLAY
			Total solutes	Fe_2O_3	
		<i>m.e./100 gm.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Kaolinite from Langley, S. C.	Untreated	2.38
	Digested 1 hour	3.80	7.5
Montmorillonite from Calif. (No. 1038)	Untreated	124.6	2.07
	Digested 1 hour	123.4	0.21
Montmorillonite from Smith Co., Miss. (No. 1019)	Untreated	108.0	4.63
	Digested 1 hour	107.5	2.0	0.36	4.36*
Nontronite from Woody District Calif.	Untreated	122.8	37.6
	Digested $\frac{3}{4}$ hour	46.1	57.3	24.9	29.7*

* Calculated as percentage of weight of sample after treatment.

The use of nascent hydrogen in place of hydrogen sulfide has several advantages in addition to being more convenient and agreeable. Sulfur is not introduced, and thus certain rather difficultly soluble iron sulfides are not formed. Also, since the color of the material being digested is the most useful criterion of the completeness of the treatment, it is desirable that the color of the suspension be not masked during treatment with the black iron sulfides.

Effect of treatment on base-exchange capacity. Obviously, any procedure for the removal of free iron oxides from soils should be as mild as possible in its action toward the clay minerals proper. As a test of this action, the effect was determined of the aluminum-ammonium tartrate digestion of kaolinite, montmorillonite, and nontronite on their base-exchange capacities (table 2).

With kaolinite clay, an increase in base-exchange capacity and considerable solution occurred. Since the kaolinite structure is such as to expose a gibbsite

sheet on one face and silica tetrahedra on the other, and since tartrate ions form an un-ionized complex with aluminum, it is probable that some aluminum was dissolved from the faces or edges of the crystal plates. The increase in exchange capacity may be interpreted to indicate a freeing of negative bonds through removal of aluminum.

The montmorillonite showed great resistance to attack by the aluminum-ammonium tartrate digestion. Since the crystal plates of this mineral consist essentially of a sheet of alumina sandwiched between two sheets of silica tetrahedra, the alumina is much less exposed and much less susceptible to the solvent action of the tartrate than in kaolinite. The slight solution noted may have been due to extraction of extraneous free oxides and possibly occasional iron ions in the montmorillonite lattice with consequent breakdown at those points.

The nontronite clay suffered great breakdown as a result of the digestion. Although the iron in nontronite is protected to some extent by its location in the middle of the layer of the three-sheet plate, such iron is apparently susceptible to reduction. The ferric ion causes some strain in the crystal lattice of nontronite due to its large size ($r = 0.67$ A.), and after reduction to the ferrous form, the ionic radius becomes still larger ($r = 0.83$ A.). This increase may exert sufficient force to cause extensive lattice disruption and consequent further exposure of the lattice iron to reduction and the solvent action of the tartrate. Although the general existence of pure nontronite in the colloid fraction of soils is considered improbable,⁴ nontronite was included in this study to illustrate the destructive action on iron-bearing clay minerals of treatments to remove free iron oxides.

Comparison of various methods for removal of iron oxides

A comparative study was made of four procedures for the removal of free iron oxides from the clay of soils. The base-exchange capacity and the chemical composition of the materials, before and after treatment, and the constituents dissolved were determined. The clay fractions used were from the B₂ horizon of Miami silt loam (Wis.), the B horizon of Cecil clay (Ala.), the B horizon of Superior clay (Wis.), and the A horizon of Lufkin clay (Ala.). The Cecil clay fraction may be characterized as kaolinitic, and the others, as montmorillonitic. Hereafter these clays will be referred to as Miami clay, Cecil clay, etc.

Four samples of each clay were treated respectively by four methods; namely, the aluminum-ammonium tartrate method here described, the H₂S-sulfuric acid method (9), the Na₂S-oxalic acid method (20), and the biological reduction method (4). The last method was slightly modified in that the fermentation was carried on in 100 ml. of a dilute plant nutrient solution, with 2 per cent dextrose added. After the anaerobic fermentation had proceeded for 5 weeks and had apparently ceased, further addition of 2.0 gm. of dextrose to each suspension was made, and the fermentation continued for a 2-week period, after which no more activity was apparent. After washing to remove dissolved iron, the biologically reduced samples were treated three times with 10 per cent hydrogen peroxide to ensure destruction of the proteinaceous material produced in the fermentation. Each treatment consisted of digestion in the peroxide solution for 24 hours.

After determination of the base-exchange capacity, following treatment by the four methods, the samples were washed twice with 95 per cent ethanol to remove salts, dried at 110°C. to constant weight in platinum crucibles, and then ignited to constant weight. Silica was determined by loss on ignition after two hydro-

TABLE 3

Effects of four methods of free iron oxide removal on the base-exchange capacity and composition of four soil clays (particles < 2 μ in diameter)

CLAYS AND METHOD OF FREE IRON OXIDE REMOVAL	BASE- EXCHANGE CAPACITY*	PORTION OF SAMPLE RECOV- ERED	CONTENT AFTER VARIOUS TREATMENTS			PORTION OF ORIGINAL SAMPLE DISSOLVED		
			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
	m.e./100 gm.	per cent	per cent	per cent	per cent	per cent	per cent	per cent
<i>Miami clay fraction</i>								
Untreated.....	59.3	65.2	20.4	11.08
Al-NH ₄ -tartrate digestion, 10 minutes.....	57.2	90.3	65.2	22.4	8.88	6.20	0.13	3.06
H ₂ S-H ₂ SO ₄ treatment.....	49.4	87.2	66.1	22.8	7.88	7.50	0.42	4.22
Na ₂ S-oxalic acid treatment...	49.3	84.6	64.5	23.3	7.01	10.63	0.61	5.16
Biological reduction.....	56.8	91.1	67.2	21.6	10.58	4.04	0.66	1.44
<i>Cecil clay fraction</i>								
Untreated.....	11.93	50.9	30.7	17.90
Al-NH ₄ -tartrate digestion, 35 minutes.....	7.75	70.7	57.7	35.8	6.10	8.68	4.53	13.44
H ₂ S-H ₂ SO ₄ treatment.....	6.07	83.7	53.1	35.1	9.23	4.85	0.28	9.92
Na ₂ S-oxalic acid treatment...	3.90	66.2	58.3	38.9	2.40	10.90	4.04	16.23
Biological reduction.....	15.0	80.4	57.0	36.6	5.87	3.44	0.21	13.02
<i>Superior clay fraction</i>								
Untreated.....	44.0	61.3	21.6	10.76
Al-NH ₄ -tartrate digestion, 30 minutes.....	40.6	88.9	57.1	22.9	8.68	8.82	1.25	3.04
H ₂ S-H ₂ SO ₄ treatment.....	30.0	88.5	61.5	18.9	7.28	6.83	4.89	4.33
Na ₂ S-oxalic acid treatment...	33.3	85.2	57.8	23.5	6.64	1.58	11.94	5.10
Biological reduction.....	36.1	83.9	64.6	19.8	9.39	6.98	4.97	2.88
<i>Lufkin clay fraction</i>								
Untreated.....	55.5	66.3	21.2	8.31
Al-NH ₄ -tartrate digestion, 15 minutes.....	52.0	88.9	67.1	22.9	6.68	6.63	0.80	2.35
H ₂ S-H ₂ SO ₄ treatment.....	45.4	88.9	67.7	20.8	4.85	5.98	2.71	4.03
Na ₂ S-oxalic acid treatment...	46.5	84.8	67.3	23.8	5.03	9.18	1.04	4.03
Biological reduction.....	49.8	84.1	66.8	21.8	6.60	10.07	2.91	2.75

* Based on original weight.

fluoric acid treatments. The residues were fused in potassium pyrosulfate, dissolved in water, and the sesquioxides precipitated with ammonia, ignited, and weighed. Iron was determined by the Jones reductor method; and aluminum, by difference. The amounts of constituents dissolved were determined by analysis of treated and untreated clays. The results are given in table 3.

A decrease in base-exchange capacity was caused by each of the treatments for the removal of free iron oxides, with the exception of the biological reduction method when applied to Cecil clay (table 3). The Na_2S -oxalic acid method removed the most iron and caused a marked reduction in exchange capacity of the clays, followed closely by the H_2S - H_2SO_4 method. The Al-NH_4 -tartrate method caused less reduction in exchange capacity than the other treatments, being appreciable only for Cecil and Superior clays. Solution of aluminum from this kaolinitic Cecil clay was considerable. The relatively small quantities of aluminum extracted from the other three clays indicate the resistance of aluminum montmorillonitic materials to this treatment. Biological reduction gave intermediate results, except that with Cecil clay it gave an increase in exchange capacity. It was noted that the fermentation with Cecil clay had the characteristic putrid odor of anaerobic processes, whereas that with the other clays had a strong yeasty odor, suggesting restricted development of anaerobes. The small amount of iron removed from the Miami sample suggests the need of further refinement in the method.

The degree of removal of red and yellow coloration from the clays was, for the most part, proportional to the completeness of iron removal. A grayish-white sample remained after complete removal of free iron oxides except with Superior clay. The Superior clay fraction had a strong red color, and contained 10.76 per cent Fe_2O_3 before treatment. This clay retained much of its original color after the treatments for removal of free iron oxides. The iron content of the clay after the sodium sulfide-oxalic acid treatment was less, however, than that of the rather white Miami clay after similar treatment. The color of the Superior clay fraction is apparently due largely to some factor other than the usual crystal-lattice iron or free iron oxides.

The Lufkin clay samples were practically pure white after all four treatments. After the Al-NH_4 -tartrate digestion, both Cecil and Miami clay, and to some degree other samples, showed a light yellowish brown color which was apparently fairly stable under continued treatment. It is suggested that this color may be due to crystal-lattice iron in the clay rather than to free oxides. Its removal by the more vigorous treatments resulted in sharp reductions in the exchange capacity, indicating breakdown of the crystal lattice, as is strikingly illustrated by Miami clay, in which 1 per cent further removal of Fe_2O_3 reduced the exchange capacity 8 m.e./100 gm. With the chemical methods, reductions in base-exchange capacity of Cecil clay are proportionately greater than loss in weight, indicating that fine and relatively active kaolinite particles were attacked.

On the basis of the amounts of iron extracted with the Al-NH_4 -tartrate digestion, it can be said with some degree of certainty that the Lufkin clay fraction contains about 2 per cent free iron oxides. The Cecil clay probably contains about 13 per cent, as judged from the biological and Al-NH_4 -tartrate methods. Allowing for some extraction of crystal-lattice iron, the free iron oxide content of the Miami clay fraction can be estimated at somewhat less than 3 per cent. No accurate estimate is possible with the Superior clay fraction, although it is probably also about 3 per cent.

EFFECT OF FREE IRON OXIDE REMOVAL ON DISPERSION OF CLAY

The need for removal of free iron oxides from soils prior to mechanical analysis has been stressed (20, 21), especially if a rather complete separation is to be made, followed by a mineralogical analysis. To measure the magnitude of this cementing action, a comparison was made of the yield of fine clay (less than 0.2μ in diameter) from four representative soils before and after treatment for the removal of free iron oxides.

Two 10-gm. samples of each soil were treated with hydrogen peroxide to remove organic matter. One sample of each soil was then given the Al-NH_4 -tartrate treatment until the soil material appeared gray, except in the case of the Coto soil, which still has a yellowish color after 90 minutes of digestion. After treatment, the samples were recovered by centrifuging, and both the treated and untreated samples were washed five times with N NaCl to saturate the base-exchange material with sodium and to remove dissolved iron from the treated samples. Excess salt was removed by washing three times with 95 per cent

TABLE 4

Effects of removal of free iron oxides on the yield of fine clay from soils

SOIL TYPE AND HORIZON	YIELD OF FINE CLAY (<0.2μ) DIAMETER, AS PERCENTAGE OF WHOLE SOIL			FREE IRON OXIDES REMOVED
	Before iron oxide removal	After iron oxide removal		
		Fine clay without iron oxides	Total fine clay (with iron oxides)	
				<i>per cent</i>
Miami silt loam, B ₂ horizon (Wis.).....	25.6	26.4	27.2	0.82
Hagerstown silt loam, B ₂ horizon (Missouri)..	25.1	31.1	33.2	2.02
Susquehanna clay, B horizon (Ala.).....	39.0	40.2	42.9	2.75
Coto clay, A horizon (Puerto Rico).....	36.3	44.1	49.3	5.19

ethanol, after which the samples were suspended in distilled water, and the fine clay was separated by means of the centrifuge (21). The process of dispersion, centrifuging, and decantation of the fine clay was repeated eight times. It was found that removal of the free iron oxides strikingly increased the amounts of fine clay obtained (table 4), i.e., 6 to 35 per cent of the yield without treatment.

BEHAVIOR OF FERRIC IRON IN BASE-EXCHANGE REACTIONS

Lutz (14) demonstrated that bentonite can take up at least twice its exchange equivalent of ferric iron, and he concluded, therefore, that the iron was held partially by adsorptive forces. Bower and Truog (6), however, in a study of exchange of common cations, obtained evidence that polyvalent cations may be held as basic ions in the exchange positions, and found that clays will take up as much as 2.5 times the exchange equivalent of ferric iron from ferric chloride solutions. Complete saturation with ferric iron as $\text{Fe}(\text{OH})_2^+$ would result in the exchange attachment of 3.0 ferric equivalents, but some competitive exchange of Fe^{++} , $(\text{FeOH})^{++}$, and H^+ from the acid ferric chloride solution probably occurs.

Fixation of exchange-iron on drying and its removal

Preliminary experiments indicated that saturation of a clay with basic ferric iron followed by drying caused a reduction in exchange capacity. This reduction was interpreted to occur as a result of iron becoming difficultly exchangeable or nonexchangeable and the corresponding exchange charges becoming nonfunctional in ordinary exchange reactions. For convenience, the iron thus held is hereinafter termed "fixed exchange-iron."

Exchange-iron fixation.—Montmorillonite, nontronite, and kaolinite clays were exchange-saturated with the basic ferric ion by washing successively three times with methyl alcohol, seven times with 0.09 per cent FeCl_3 solution in methyl alcohol, twice with methyl alcohol, and finally twice with benzene. To prevent the clay from drying in hard aggregates (11), benzene was used as the medium from which the clays were dried. The samples were dried at 110°C . overnight and dispersed in distilled water by means of a rubber plunger, and the exchange capacity was redetermined. The excess NH_4Ac displacing solution was subsequently removed by ethanol washings.

Drying after saturation with iron resulted in a decrease in exchange capacity of all three clays (table 5). The amount of reduction was proportionately much larger for the montmorillonite (23 per cent) and the nontronite (35 per cent) than it was for the kaolinite (8.5 per cent).

Removal of fixed exchange-iron.—Three kinds of treatment were employed to free the exchange spots rendered nonfunctional by fixation of exchange-iron: (a) Removal of the iron by the Al-NH_4 -tartrate treatment described; (b) boiling for 30 minutes in alkaline solution of 2 per cent Na_2CO_3 , which should transform the iron completely to ferric hydroxide; (c) treatment with a solution of sodium tartrate in contact with metallic aluminum, in which case the pH rises rapidly during the digestion and which should combine the effects of the (a) and (b) treatments.

With Al-NH_4 -tartrate digestion, the base-exchange capacity of montmorillonite was only partly restored and that of kaolinite was increased over the original (table 5). The latter effect was also noted previously with ordinary kaolinite after Al-NH_4 -tartrate digestion. With digestion in sodium carbonate solution, the base-exchange capacities of both montmorillonite and nontronite were partly restored and that to kaolinite was still further increased over the original. The latter result may have been due to the extraction of occasional aluminum ions from the surfaces and edges of the kaolinite plates. Digestion with sodium tartrate in contact with metallic aluminum resulted in complete recovery of the original base-exchange capacity of montmorillonite and partial recovery of that of nontronite, as calculated on the original weight basis.

Physical vs. chemical blocking of base-exchange positions

It has been suggested (20) that the increases in base-exchange capacity that result from the removal of free iron oxides from clays may be due to elimination of a mechanical blocking or encasing effect exerted by these oxides at the base-exchange areas. To determine whether this is true, ferric oxide was introduced into two montmorillonite suspensions in different ways: Ten milliliters of FeCl_3

solution (1.34 per cent Fe_2O_3) was added (a) to an ammoniacal suspension of 0.35 gm. montmorillonite, so that the iron was immediately and intimately precipitated on the clay as ferric hydroxide (opportunity for physical effect, without opportunity for exchange attachment), and (b) to an acid suspension of the montmorillonite (pH 2), after which the pH of the suspension was slowly raised to slightly above pH 7.0 by the addition of 0.25 N NH_4OH so that the ferric ion might be absorbed in an exchange reaction (opportunity for chemical effect.) In both cases the samples were washed twice with N NH_4Ac of pH 7.0 and then washed and dried as in exchange-iron fixation tests. The exchange capacities found were 107.7 and 97.6 respectively as compared to 108.0 m.e./100 gm. for the untreated montmorillonite. These results indicate that increased base-exchange capacity

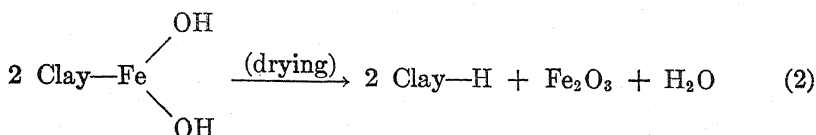
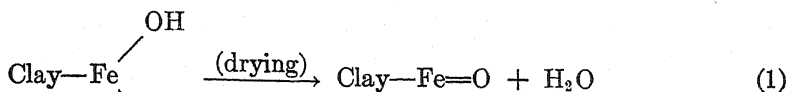
TABLE 5
Effect on base-exchange capacity of fixation of exchange-iron and its removal

SPECIAL TREATMENT	BASE-EXCHANGE CAPACITY CALCULATED ON ORIGINAL WEIGHT		
	Montmorillonite	Nontronite	Kaolinite
	m.e./100 gm.	m.e./100 gm.	m.e./100 gm.
None (check).....	124.6	129.1	2.62
Exchange-iron fixation (sample iron-saturated and dried).....	95.8	84.2	2.40
Fixation of exchange-iron and then treatment as follows:			
(a) Digestion with aluminum-ammonium tartrate for 2 minutes.....	110.9	3.42
(b) Digestion with 2 per cent Na_2CO_3 solution for $\frac{1}{2}$ hour.....	108.5	99.6	4.08
(c) Digestion with aluminum-sodium tartrate for $1\frac{1}{2}$ hours.....	124.5	110.5

of soils and clays following removal of iron oxide is due to removal of chemically held iron, rather than elimination of physical obstruction to exchange.

Release of exchange-iron from clay on drying

Although the base-exchange material may become saturated with $\text{Fe}(\text{OH})_2^+$ to the extent of 90 per cent of the exchange capacity (6), it is apparent that only part of the iron absorbed in the cation-exchange positions can be fixed, and that the remaining exchange charges remain functional (table 5). It is postulated that, of the two different types of base-exchange charges in the montmorillonite group of clay minerals—one type arising in the gibbsite layer from the substitution of Mg^{++} for Al^{+++} , and the other in the sheets of silica tetrahedra from the substitution of Al^{+++} for Si^{++++} (15), one type, reaction (1) below, is able to fix the exchange-iron and become nonfunctional in ordinary cation exchange, whereas the other, reaction (2), is not.



The occurrence of reaction (1) has already been substantiated (table 5).

In a test of whether reaction (2) occurs, two equal samples of montmorillonite were saturated with $\text{Fe}(\text{OH})_2^+$ as described previously. One sample was then stored moist while the other was dried overnight at 110°C . Both samples were

TABLE 6

Base-exchange capacity of soil clays before and after aluminum-sodium tartrate digestion

SOURCE OF SOIL CLAY	BASE-EXCHANGE CAPACITY BASED ON ORIGINAL WEIGHT		INCREASE DUE TO TREATMENT	Fe_2O_3 EXTRACTED
	Before treatment	After treatment		
	m.e./100 gm.	m.e./100 gm.	per cent	per cent
Spencer silt loam, B ₂ (Wis.).....	63.0	69.6	10.5	0.74
Lufkin clay, A (Ala.).....	55.0	61.3	11.4	1.13
Miami silt loam, B ₂ (Wis.).....	59.3	66.2	11.6	1.30
Carrington silt loam, B ₂ (Wis.).....	46.9	56.7	20.9	1.31
Cecil clay, B (Ala.).....	11.9	18.9	58.8	0.61

redispersed in equal volumes of distilled water. Determinations of the pH of the suspensions, by means of the glass electrode, gave pH 2.73, and 3.60, respectively, for the dried and undried samples. This striking reduction in pH as a result of drying substantiates the occurrence of reaction (2). The rather low pH of the undried sample can be attributed to competitive absorption of the H^+ from the acid ferric chloride saturating solution. In this reaction the iron is released by drying and the cation-exchange position is saturated with exchangeable hydrogen; this iron, though difficultly soluble, is excluded from the phrase "fixed exchange-iron," as herein used.

Estimation of fixed exchange-iron in soil clays

To determine the extent to which fixed exchange-iron occurs in soils, clay samples from five soils were digested for 1 hour with sodium tartrate in contact with metallic aluminum as previously described. The base-exchange capacity rendered active by treatment varied from 10 to 59 per cent of the original exchange capacity (table 6). The increases were probably due to the removal of fixed exchange-iron, since this treatment did not increase the base-exchange

capacity of montmorillonite except when such capacity had previously been reduced by iron fixation. With Cecil clay, some of the increase may simulate that observed with the pure kaolinite. The small amounts of iron removed (table 6) indicate that, though the Al-Na-tartrate treatment is specific for removal of fixed exchange-iron, it is not so well adapted to the complete removal of free iron oxides as the Al-NH₄-tartrate procedure.

INFLUENCE OF FREE IRON OXIDE REMOVAL ON X-RAY DIFFRACTION PATTERNS

To test whether the Al-NH₄-tartrate digestion caused any fundamental change in the crystalline nature of the clay minerals, original and treated clays were prepared for x-ray diffraction analysis according to the procedure described by Jackson and Hellman (11) using more recent modifications (1, 10) designed to give controlled hydration.

Results with soil clays

With Superior clay and Lufkin clay the treatment resulted in a more intense and more sharply defined 16 Å. diffraction line corresponding to the (001) spacing characteristic of montmorillonite. The very weak 10 Å. diffraction line, indicative of the presence of some mica-like minerals, was unchanged in intensity by the treatment. With the Miami (Wis.) clay there is a slight decrease in intensities of both the 16 Å. montmorillonite line and the faint line at 10 Å. as a result of treatment, probably due to some disruption of the iron clay lattices. None of the patterns of these montmorillonitic clays shows diffraction lines characteristic of iron oxides. The x-ray diffraction pattern of treated Cecil clay showed a decrease in background fog, an increase in the definition and intensity of diffraction lines, and the appearance of a disc-like line of weak intensity at about 16 Å. (montmorillonite, 5 per cent), which is not apparent in the pattern of the untreated material. In addition, the diffraction lines of hematite at 2.71, 2.51, 2.21, and 1.70 Å. were eliminated as a result of treatment. The x-ray diffraction patterns thus indicate that the Al-NH₄-tartrate treatment does not seriously affect the crystalline nature of the clay minerals and that the removal of free iron oxides may be desirable in x-ray diffraction analysis of certain types of clays.

Results with ferric oxide-montmorillonite systems

The improvement obtained in x-ray diffraction patterns of soil clays as a result of the removal of free iron oxides, particularly the intensity and sharpness of the characteristic montmorillonite line, indicates a more regular organization of the crystal lattice plates once these are freed from iron oxide coatings. Hence, the effect on x-ray diffraction patterns of the introduction of ferric iron into montmorillonite and its subsequent removal was investigated. Montmorillonite samples were prepared by methods described earlier to represent: (a) untreated, (b) iron-saturated but not dried, (c) iron-saturated and dried, and (d) iron-saturated and dried, followed by iron removal by Al-NH₄-tartrate digestion. These samples were then prepared for x-ray diffraction analysis by methods mentioned earlier (10, 11), which involve saturation with calcium of functional exchange charges by Ca(Ac)₂ washings of pH 7.7.

The most striking difference in the diffraction patterns was the decrease in intensity and sharpness of the 16 Å. line of the dried iron-saturated sample (c). Apparently, fixed exchange-iron interferes with the orderly orientation of the montmorillonite crystal plates during the sample preparation for x-ray diffraction analysis. Despite the presence of ferric oxide precipitated as the hydroxide in the clay sample (b) by the $\text{Ca}(\text{Ac})_2$ washings, the diffraction pattern was almost as sharp and intense as that of the untreated material. Removal of the fixed exchange-iron from sample (d) by Al-NH_4 -tartrate digestion resulted in a sharp, intense 16 Å. line and a satisfactory diffraction pattern, indicating restoration of proper orientation of the crystal plates. These results, thus, partly explain the improvement of x-ray patterns of soil clays resulting from prior treatment to remove free iron oxides.

SUMMARY

A modification was developed in the method of Jeffries for reduction and solution of free iron oxides from soils and clays by means of nascent hydrogen. The sample is boiled in 10 per cent ammonium tartrate solution in contact with metallic aluminum. Ammonia formed volatilizes, thus stabilizing the solution at a favorable reaction of approximately pH 6.4. A relatively short digestion time (usually 15 to 45 minutes) suffices, during which attack on montmorillonite, kaolinite, muscovite, and hydrous mica is unappreciable to slight unless the lattices contain notable amounts of ferric iron. The method is decidedly less destructive to these lattices than earlier methods. With pure nontronite, the lattice is markedly attacked by this or other methods because of ease of reduction of the crystal lattice ferric iron present. The use of nascent hydrogen instead of hydrogen sulfide for reduction of ferric oxide avoids the formation of iron sulfides, which mask observation of the course of the reaction and tend to become difficulty soluble.

Removal of free iron oxides, which tend to aggregate clay particles, resulted in increases of 6 to 29 per cent in the amounts of fine clay mechanically separated from four soils.

Drying base-exchange material containing exchangeable basic ferric iron ($\text{clay-Fe} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$) caused fixation of part of the exchange-iron ($\text{Clay} - \text{Fe} = \text{O}$).

The base exchange charges thus involved became nonfunctional, but were re-activated on displacement of the fixed exchange-iron by digestion in an alkaline solution of sodium tartrate. With the clay fractions of Carrington, Miami, Spencer, Lufkin, and Cecil soils, increases in base-exchange capacity due to removal by this treatment of fixed exchange-iron ranged from 10 to 59 per cent of their base-exchange capacities before treatment.

The x-ray diffraction patterns of soil clays made after removal of free iron oxides were usually sharper and more intense than patterns of the untreated clays. The x-ray diffraction lines of montmorillonite containing fixed exchange-iron were less sharp than those of untreated montmorillonite, but were fully as sharp after removal of the fixed exchange-iron.

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A MODIFIED METHOD FOR DETERMINING BASE-EXCHANGE CAPACITY OF SOILS

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Many methods have been proposed for the determination of base-exchange capacity of soils. Most of the proposed methods are somewhat the same in principle, that is, the soil is leached with a salt solution, the excess saturating solution is washed out with methyl or ethyl alcohol, and the adsorbed cation is replaced and determined. Chapman and Kelley (1) found that NH_4 may be lost from the exchange complex as a result of washing with an excess of methyl alcohol. When the acidity of the alcohol was neutralized with NH_4OH , however, no such loss occurred. In order to eliminate the necessity of washing with methyl alcohol, Chapman and Kelley determined the excess saturating solution after the soil had been saturated with NH_4 by the use of NH_4Cl . They determined the NH_4 and Cl in the sample and by difference calculated the amount of NH_4 in the exchangeable form. They found close agreement between results by this method and those obtained by washing with neutral methyl alcohol.

This investigation was undertaken with the idea of developing a simple procedure which would eliminate the necessity for washing out the excess saturating solution. In the modified method, which follows, the quantity of excess saturating solution is determined by subtracting the dry weight of the funnel, filter paper, and sample from the weight of the combination after the sample has been leached first with a N solution of the saturating salt and then with a 0.1 N solution of the salt. The excess 0.1 N solution and the adsorbed cation are leached out and determined. The total cation minus that present as 0.1 N solution is equal to the base-exchange capacity. Any saturating solution may be used if the saturating cation lends itself readily to chemical determination.

METHODS AND MATERIALS

The modified method for determining base-exchange capacity using barium acetate as the saturating solution is as follows: Weigh a quantity of soil equivalent to 1 to 2.5 m.e. of exchange capacity into a 150-ml. beaker. Add approximately 25 ml. of a N solution of barium acetate to the soil. After the sample has stood an hour with intermittent stirring, wash it into a weighed funnel and filter paper. Leach the sample with a total of 250 ml. of a N barium acetate solution containing 0.5 per cent n -butyl alcohol intermittently over a period of approximately 24 hours. Then leach with 250 ml. of 0.1 N solution containing 0.5 per cent n -butyl alcohol over a period of 24 hours. At least 100 ml. of the 0.1 N solution should be put through during the last 2 or 3 hours of leaching. When the last portion of 0.1 N solution drains through, weigh the funnel containing the sample and filter-paper. The weighing may be done rapidly and with sufficient accuracy with a torsion balance having a sensitivity of 0.1 gm. Care

should be taken to wash the sides of the funnel and the top of the filter paper well with the 0.1 *N* solution. The weight of the funnel, filter paper, and sample after being washed with 0.1 *N* solution minus the dry weight of the combination is equal to the milliliters of excess 0.1 *N* solution in the sample. Leach out the excess 0.1 *N* barium acetate solution and the adsorbed barium with 250 ml. of approximately 0.2 *N* HCl and determine the total barium present. The total barium minus the quantity present as 0.1 *N* solution is equal to the exchange capacity. The barium is determined in the following manner using tetrahydroxyquinone as an internal indicator (6): To a 25-ml. aliquot add 0.05 *N* K₂SO₄ solution slightly in excess of that necessary to precipitate the barium. Titrate to the end point of phenolphthalein with NH₄OH (1 + 1). If the extract is likely to contain more than 60 p.p.m. of phosphorus, brom cresol green should be used instead of phenolphthalein. Add 35 ml. of 95 per cent alcohol and 2 ml. of 0.25 *N* AgNO₃. Titrate the excess sulfate to the end point of the THQ sulfate indicator with 0.05 *N* BaCl₂. The indicator changes from yellow to a permanent rose-red color at the end point. One dipper of THQ should be added at the beginning of the titration and another one toward the end of the titration. This method of determining barium checks well with the standard gravimetric method of determining barium as barium sulfate.

Base-exchange capacity was run by saturating with calcium acetate and ammonium acetate in the above manner. When calcium acetate was used, calcium was determined by precipitating the calcium as the oxalate and titrating with standard KMnO₄. In the case of ammonium acetate the NH₃ was distilled over into boric acid and titrated with standard HCl.

For comparison with the modified method, base-exchange capacity was determined by washing out the excess saturating solution with 80 per cent alcohol. The alcohol was neutralized with the base of the particular cation used for saturating the soil, except in one case where barium acetate adjusted to pH 5.0 was used as the saturating solution. This method will be designated as the "standard method" throughout the paper regardless of the saturating solution used.

All data, except some of those in tables 4 and 5, were obtained by using saturating solutions containing 0.5 per cent *n*-butyl alcohol.

The soils used in this study range from sands to peats. Some of the sands were developed under conditions of poor drainage and, as a result, contain considerable organic matter and therefore a rather high base-exchange capacity.

RESULTS

A comparison of the modified method of determining base-exchange capacity with the "standard method" is presented in table 1. The data show that there is no appreciable difference between the two methods when neutral barium acetate is used as the saturating solution. When neutral ammonium acetate is used as the saturating solution the "standard method" gives lower values for six of the nine soils. Since Ba⁺⁺ is more strongly adsorbed by the exchange complex than is NH₄⁺, it is less likely to be lost by hydrolysis and subsequent removal

by the alcohol washings. Also, in some cases the alcohol washing dissolved considerably more organic matter from the NH_4 -saturated soils than from the Ba-saturated soils. The dissolution of organic matter from the NH_4 -saturated soils may have caused low results with the "standard method."

It is frequently desirable to determine base-exchange capacity at some pH other than 7.0. The data in table 2 show the results of the two methods for

TABLE 1

Comparison of the modified method of determining base-exchange capacity with the standard method using neutral saturating solutions

SOIL TYPE	BASE-EXCHANGE CAPACITY* AS MEASURED BY NEUTRAL BARIUM ACETATE SOLUTION		BASE EXCHANGE CAPACITY AS MEASURED BY NEUTRAL AMMONIUM ACETATE SOLUTION	
	Modified method	Standard method	Modified method	Standard method
	m.e.*	m.e.	m.e.	m.e.
Leon sand.....	7.9	8.0	5.5	5.6
Fellowship fine sandy loam.....	11.8	11.4	8.4	7.8
Portsmouth sand.....	22.8	23.0	14.5	12.6
Bayboro clay loam.....	45.3	46.4	32.0	29.7
Orangeburg fine sandy loam.....	7.7	8.0	5.3	5.5
Norfolk sand.....	4.5	4.2	2.9	3.1
Brighton peat.....	135.7	135.0	95.3	91.0
Everglades peat.....	240.0	240.0	144.1	133.0
Okeechobee muck.....	114.0	112.8	84.5	76.5

* In this and all subsequent tables, m.e. = m.e. per 100 gm. soil.

TABLE 2

Comparison of the modified method of determining base-exchange capacity with the standard method using a barium acetate solution adjusted to pH 5.0

SOIL TYPE	BASE-EXCHANGE CAPACITY		
	Modified method	Washed with 80 per cent alcohol—pH 5.0	Washed with 80 per cent alcohol—pH 7.0
	m.e.	m.e.	m.e.
Leon sand.....	5.5	6.0	6.0
Fellowship fine sandy loam.....	7.6	8.8	9.0
Portsmouth sand.....	16.8	19.0	18.5
Bayboro clay loam.....	29.4	35.6	35.6
Orangeburg fine sandy loam.....	5.4	5.4	5.8
Norfolk sand.....	2.9	2.9	2.7
Brighton peat.....	96.7	106.8	105.6

barium acetate adjusted to pH 5.0. In most cases the "standard method" gives higher values than the modified method. According to the data it makes little difference whether the 80 per cent alcohol used with the "standard method" is adjusted to pH 5.0 or pH 7.0. It is interesting to note that the base-exchange capacity as measured by barium acetate at pH 5.0 is only about 70 per cent as great on the average as the base-exchange capacity at pH 7.0.

To test the method further, three concentrations of barium acetate were used to wash out the neutral *N* barium acetate. The data are reported in table 3. The exchange values for the three concentrations used are very similar, though those for the 0.2 *N* barium acetate are slightly higher in all but one case. A relatively low concentration should be used in order to keep the barium content

TABLE 3

Effect of the concentration of the second 250-ml. portion of barium acetate leached through in the modified method on base-exchange capacity

SOIL TYPE	BARIUM ADSORBED		
	Normality of second 250-ml. portion of barium acetate		
	0.05 <i>N</i>	0.1 <i>N</i>	0.2 <i>N</i>
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
Leon sand.....	7.6	7.9	7.9
Fellowship fine sandy loam.....	11.5	11.8	12.6
Portsmouth sand.....	22.9	22.8	23.5
Bayboro clay loam.....	45.1	45.3	45.8
Orangeburg fine sandy loam.....	7.9	7.7	8.6
Norfolk sand.....	4.3	4.5	4.8
Brighton peat.....	135.5	135.7	137.7

TABLE 4

*Influence of *N*-butyl alcohol and time of leaching on the base-exchange capacity as measured by neutral barium acetate**

SOIL TYPE	BARIUM ADSORBED					
	Time of intermittent leaching with barium acetate solutions			Time of intermittent leaching with barium acetate solutions containing 0.5 per cent <i>n</i> -butyl alcohol		
	5 hrs.	44 hrs.	90 hrs.	5 hrs.	20 hrs.	44 hrs.
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
Leon sand.....	5.8	6.7	6.8	6.5	7.9	7.9
Fellowship fine sandy loam.....	7.9	10.2	11.2	9.4	11.6	11.8
Portsmouth sand.....	17.4	19.6	20.4	20.8	21.1	22.8
Bayboro clay loam.....	36.9	41.8	44.0	42.3	43.7	45.3
Orangeburg fine sandy loam.....	5.9	6.9	7.6	5.8	7.7	7.7
Norfolk sand.....	2.7	3.7	3.9	3.7	3.7	4.5
Brighton peat.....	115.2	130.6	134.8	121.0	130.0	135.5

* Modified method.

in the excess solution low in comparison to the quantity of adsorbed cation.

Schollenberger and Dreibelbis (5) suggested that the time of contact of soil with the saturating solution may influence the magnitude of the exchange capacity. To study the effect of time of leaching on base-exchange capacity, several soils were leached intermittently for 5, 44, and 90 hours. The same volume of

barium acetate was used in each case. In most instances there was an appreciable increase in barium adsorption with increasing time of leaching. The data are presented in table 4. Part of the increase in exchange capacity with time may be due to more thorough wetting and greater penetration of the solution into the soil particles. To study this point *n*-butyl alcohol was added to the barium acetate solution at the rate of 0.5 per cent, and the same soils were leached for 5, 20, and 44 hours. The addition of *n*-butyl alcohol resulted in higher exchange capacity for comparable leaching time. The fact that *n*-butyl alcohol lowers the surface tension of the solution may account for the more rapid equilibrium between the soil and solution as a result of more rapid wetting. Mehlich (4) found that barium adsorption was greater with longer contact between the soil and saturating solution.

TABLE 5

*Influence of N-butyl alcohol and time of leaching on base-exchange capacity as measured by neutral ammonium acetate**

SOIL TYPE	NH ₄ ADSORBED			
	Time of intermittent leaching with ammonium acetate solutions		Time of intermittent leaching with ammonium acetate solutions containing 0.05 per cent <i>n</i> -butyl alcohol	
	5 hrs.	90 hrs.	5 hrs.	44 hrs.
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
Leon sand.....	5.7	5.1	6.0	5.5
Fellowship fine sandy loam.....	8.7	8.6	7.9	8.4
Portsmouth sand.....	13.5	13.7	14.3	14.5
Bayboro clay loam.....	30.0	31.1	31.6	32.0
Orangeburg fine sandy loam.....	6.2	6.0	5.1	5.3
Norfolk sand.....	2.6	2.7	2.8	2.9
Brighton peat.....	90.0	91.5	94.0	95.3
Everglades peat.....	128.0	127.7	145.6	144.1
Okeechobee muck.....	76.0	77.2	84.7	84.5

* Modified method.

The same type of study was made using ammonium acetate. The data, reported in table 5, show that the base-exchange capacity did not change with time of leaching, and the addition of *n*-butyl alcohol had little effect in most cases. Since neutral ammonium acetate caused considerable dispersion, equilibrium between the soil and the saturating solution was probably established rather quickly without the addition of *n*-butyl alcohol.

Golden *et al.* (2) found that various saturating solutions gave a wide range in exchange capacity for several Maryland soils. Ammonium acetate, for example, gave only about 60 per cent as high exchange capacity as barium acetate. They concluded that potassium and barium acetates were the best for estimating total exchange capacity.

The exchange values for the nine Florida soils studied, as measured by the modified method using neutral calcium acetate solution, were found to be as follows:

SOIL TYPE	BASE-EX- CHANGE CAPACITY m.e.
Leon sand.....	8.4
Fellowship fine sandy loam.....	12.6
Portsmouth sand.....	21.5
Bayboro clay loam.....	44.4
Orangeburg fine sandy loam.....	8.4
Norfolk sand.....	5.5
Brighton peat.....	136.0
Everglades peat.....	245.3
Okeechobee muck.....	120.4

These data in comparison with those reported in table 1 show that calcium and barium acetates give virtually the same exchange values for these soils whereas ammonium acetate gives much lower values. Calcium should come nearest to giving the true base-exchange capacity of a soil, since it is the dominant base in most soils. Since barium is easy to determine and gives about the same exchange capacity as calcium, it appears to be a satisfactory cation to use for determining base-exchange capacity of Florida soils. As pointed out by Kelley (3) there is a possibility that barium may be held in the soil in a nonreplaceable form by such substances as colloidal SiO_2 , Al_2O_3 , and Fe_2O_3 . On the other hand, barium acetate has less solvent action on organic matter than ammonium acetate, and this factor probably outweighs the possible disadvantage of barium of forming insoluble compounds.

DISCUSSION

The modified method as outlined can be used for any type of saturating solution provided the saturating cation can be accurately determined. The soils used in this study were easy to filter, and therefore ordinary filtering funnels were used. For heavier soils Hirsch filtering funnels or small Büchners with suction work satisfactorily.

For the soils studied the method of determining barium by titrating to the end point of THQ sulfate indicator compared favorably with the standard gravimetric method for determining barium. Enough phosphate may dissolve from soils high in phosphate to interfere with the titration. The presence of too much phosphate would precipitate some barium and lead to low results. It is doubtful if many soils contain enough acid-soluble phosphorus to interfere to an appreciable extent.

A very small error is involved in determining the excess saturating solution by weight differences. The weight of the adsorbed cation is figured as a part of the weight of excess saturating solution. For example, in the case of barium, the weight of 1 m.e. of adsorbed barium would be 0.068 gm. If the original soil was hydrogen-saturated and 0.1 N barium acetate was used as the final leaching solution, a negative error of 0.67 per cent would result. If the original soil

sample was calcium-saturated there would be a negative error of 0.48 per cent. An error of this magnitude is negligible.

When this study was initiated, 0.1 *N* was adopted as the concentration of the final saturating solution in the modified method; therefore, most of the data presented were obtained by using 0.1 *N* solutions. The data in table 3 show that there is no appreciable difference in exchange values when 0.05, 0.1, or 0.2 *N* barium acetate solutions are used. From the analytical standpoint it is well to keep the quantity of excess cation as low as possible in comparison to the adsorbed cation. For routine base-exchange determinations 0.05 *N* solutions should be used as the final saturating solution.

SUMMARY

A modified method for determining base-exchange capacity of soils has been described which eliminates the necessity of washing out the excess saturating solution. In the modified method as outlined the soil sample is leached first with 250 ml. of a *N* solution of the saturating salt and then with 250 ml. of a 0.1 *N* solution of the salt. The quantity of excess 0.1 *N* solution is determined by subtracting the dry weight of the funnel, filter paper, and sample from the weight of the combination after the sample has been leached with the 0.1 *N* solution. The excess 0.1 *N* solution and the adsorbed cation are leached out with 0.2 *N* HCl and the total quantity of the cation is determined. The total cation minus that present as excess 0.1 *N* solution is equal to the base-exchange capacity. The method may be used with any saturating solution provided the saturating cation can be determined accurately.

When neutral barium acetate was used as the saturating solution the modified method gave the same results as the "standard method" (washing with 80 per cent alcohol). When neutral ammonium acetate was used, however, the modified method gave higher results in most cases. When barium acetate adjusted to pH 5.0 was used as the saturating solution, the modified method gave lower results in most cases than the "standard method."

Base-exchange capacity increased appreciably with time of intermittent leaching when barium acetate was used. The addition of 0.5 per cent of *n*-butyl alcohol to the barium acetate solution lowered the leaching time necessary to obtain equilibrium between the soil and the saturating solution. When ammonium acetate was used as the saturating solution, base-exchange capacity did not change appreciably with time of leaching or with the addition of *n*-butyl alcohol.

Nine Florida soils showed about the same exchange capacity as measured by calcium or barium. Base-exchange values as measured by ammonium were only 65 per cent as high on the average as the calcium and barium values.

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A RAPID METHOD OF CALIBRATING VARIOUS INSTRUMENTS FOR MEASURING SOIL MOISTURE IN SITU

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There are a number of methods for measuring soil moisture *in situ*. The method used depends upon the moisture range involved. Whether or not it is necessary to construct a calibration curve for a particular instrument for various moisture contents of any given soil often depends upon the information desired and upon the method used. Even though in a few cases such calibration curves are not essential, they are generally beneficial and in most cases would be determined if some simple, accurate method for obtaining them were available. The following paper deals with a simple method of calibration.

In following soil moisture changes on an irrigation experiment with guayule, several methods were used. Among these was the plaster of paris block method described by Bouyoucos (2). When the blocks were first purchased, an attempt was made to calibrate them by the Bouyoucos method. Very unsatisfactory results were obtained, because of either poor technique or an inherent error in the method. Anderson and Edlefsen (1) present data that show there is a tremendous lag in calibrating plaster of paris blocks by this method. They came to the conclusion that a satisfactory calibration curve can be obtained only by placing the block "in a soil surrounded by roots of actively transpiring plants and then observing the relationship between soil moisture content and the block resistance." They considered it essential to do this in order to obtain a uniform soil moisture content. Calibrations obtained in this way require considerable time, space, and labor.

PROCEDURE

It was thought that the same results could be obtained more simply by a different procedure. One was devised for calibrating the units by embedding them in a representative sample of soil, using a technique similar in several respects to that described by Shaw and Bayer (4). The soil was placed in a wire basket ($\frac{1}{4}$ -inch mesh) of dimensions $1\frac{1}{2}$ by $2\frac{3}{8}$ by $3\frac{1}{2}$ inches. The inside of the basket was lined with cloth (unbleached muslin). The electrode was centrally located in the soil, leaving $\frac{1}{2}$ inch of soil on all sides of the electrode. The soil was completely wet by capillarity and then placed into a humidity chamber (relative humidity 93 to 98 per cent) to drain. After 48 hours it was removed and placed on a $\frac{1}{4}$ -inch mesh wire support which allowed evaporation from all sides. After 5 hours it was again put into the humidity chamber and allowed to remain there 19 hours, after which it was removed, weighed, and the resistance of the

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unit determined. It was again left on the wire stand for 5 hours, then put into the humidity chamber for 19 hours, removed, weighed, and the resistance of the unit determined as before. This procedure was continued until the soil no longer lost moisture when exposed to the air. In the humidity chamber evaporation was retarded and opportunity was presented for moisture conditions throughout the block to approach equilibrium.

RESULTS AND DISCUSSION

When the above procedure was used, smooth and reproducible curves were obtained. An example is given in figure 1A. The soil used was Chualar loam. It has a "field capacity" and wilting point of 16 per cent and 6 per cent, respectively,

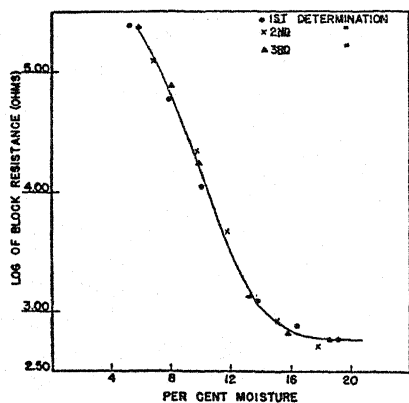


FIG. 1A

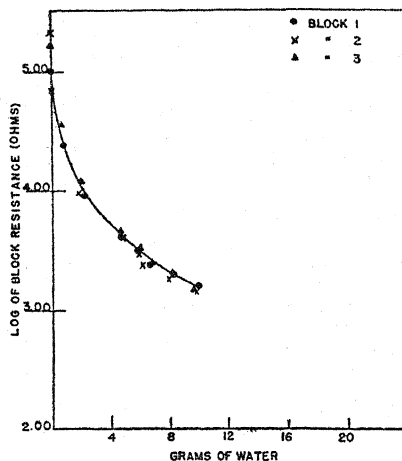


FIG. 1B

FIG. 1A. Calibration curve of Chualar loam obtained by three separate determinations, using different plaster of paris blocks.

FIG. 1B. Calibration curve obtained on three plaster of paris blocks without soil.

as determined by the methods of Veihmeyer (5)². In a calibration of this type it is necessary to subtract the water in the plaster of paris block at any given resistance. This is done in order that the water held by the block will not be included with that held by the soil, thus giving an apparent increase in soil moisture percentage. The resistances of the plaster of paris blocks vs. grams of water held by the blocks at various resistances are given in figure 1B. This curve was used in making subtractions for the amount of water held by the plaster of paris block at various resistance readings.

It could be possible to obtain reproducible curves such as those given in figure 1A and still have a large differential moisture content between the center and the outer layers of the soil sample. In order to ascertain whether or not this was the case, a number of duplicate soil samples were prepared in wire baskets in

² Veihmeyer, F. J. Method of determining permanent wilting percentages of soils. Univ. of Calif., Col. of Agr., Davis, Calif. Correspondence.

the manner previously described except that the plaster of paris blocks were omitted. The treatment given these soil blocks was the same as that described for the calibration of the plaster of paris blocks. At intervals of a few days, when the soil blocks were removed from the humidity chamber one was selected at random, the wire basket and cloth were removed, and a slice approximately $\frac{1}{4}$ inch thick was pared from each of the four vertical surfaces, leaving a block 1 by $1\frac{7}{8}$ by $3\frac{1}{2}$ inches. For moisture determination the block was then sectioned horizontally into seven layers, each $\frac{1}{2}$ inch thick. The $\frac{1}{4}$ -inch slices were removed from the vertical surfaces in order to eliminate, as nearly as possible, the masking effect of a dry layer all around the subsequent samples in case

TABLE 1

Percentage moisture in various portions of soil block that was wetted, then alternately dried 5 hours under laboratory conditions and placed in humidity chamber for 19 hours

DETERMINATION	DAYS AFTER WETTING	SOIL LAYERS								WEIGHTED AVERAGE, ENTIRE BLOCK
		1	2	3	4	5	6	7	Outside*	
1	..	6.2	6.5	6.8	6.8	6.8	6.4	6.4	6.6
2	4	15.2	17.0	17.9	17.8	18.8	17.8	16.4	17.3
3	7	14.3	14.1	13.6	14.3	14.1	14.0	14.6	14.1
4	10	10.3	11.3	9.1	10.3	10.9	10.1	10.6	10.4
5	15	2.8	3.2	3.6	3.7	3.9	3.9	3.5	3.6
6	19	1.4	1.6	1.7	1.9	1.9	1.9	1.7	1.7
7	3	12.0	14.5	15.0	15.0	14.7	16.2	16.9	15.0
8	7	6.2	6.2	6.2	6.2	6.3	6.3	6.5	6.3
9	0	21.1	21.8	23.2	23.2	22.9	22.9	23.1	23.6	23.1
10	2	14.5	17.7	18.2	17.9	17.2	17.6	19.0	17.3	17.4
11	3	14.0	15.4	15.2	15.3	15.9	16.4	15.0	13.9	14.7
12	4	14.2	17.2	15.5	13.9	13.7	14.7	14.3	14.0	14.4
13	6	6.9	7.8	7.9	7.8	7.6	8.3	7.6	7.9	7.8
14	7	7.6	8.2	7.7	7.5	6.3	7.0	7.4	6.6	7.1
15	9	5.4	5.5	5.5	5.2	5.3	5.3	5.5	5.2	5.3
16	10	5.4	5.8	5.8	5.8	5.7	5.8	5.9	5.4	5.6
17	11	2.3	2.9	3.3	3.3	3.3	3.2	2.8	2.1	2.6
18	12	1.4	1.7	1.8	1.9	1.8	1.7	1.5	1.3	1.5

* Outside layer refers to the material pared from the four vertical surfaces of the blocks.

such a dry layer existed. With this procedure, any large differential in moisture content from the outside to the center of the soil block should show up in the moisture content of the various layers. The seven $\frac{1}{2}$ -inch layers are numbered consecutively from top to bottom. In table 1 are given the data obtained from 18 individual determinations. It is seen that the very top layer, no. 1, is usually the driest but that there are no large differences in moisture content of the various layers. As small as this lag was, it is probable that if the blocks had been left in the humidity chamber longer, the difference would have been still less.

It was thought that perhaps it would not be necessary to place the soil blocks in a humidity chamber at all in order to obtain satisfactory calibration curves for field use. Calibrations were made in which the soil, after being wet by capil-

larity, allowed to drain in a humidity chamber, and then removed from the humidity chamber, was left under laboratory conditions until dry. These calibration curves were smooth, but were not entirely reproducible. Soil blocks were treated in this same way and then divided for moisture determinations as indicated earlier. The results of several determinations are given in table 2. There is considerable variation in the soil moisture content of the various layers, especially at the lower moisture contents. Evidently at the higher moisture values the movement of the water in the soil is sufficiently rapid to keep the entire block at a nearly uniform moisture content, but at lower moisture levels

TABLE 2

Percentage moisture in various portions of soil block exposed to laboratory conditions continuously

DETERMINATION	HOURS*	SOIL LAYERS								WEIGHTED AVERAGE, ENTIRE BLOCK
		1	2	3	4	5	6	7	Outsidet	
1	24	22.1	22.6	22.3	22.0	22.6	22.5	21.5	22.5	22.4
2	48	13.6	13.9	13.8	13.6	13.7	14.0	13.7	14.0	13.9
3	72	4.8	6.5	7.1	7.4	7.4	7.2	6.6	4.3	5.5
4	96	1.9	2.4	3.0	3.3	3.3	2.8	2.0	1.7	2.2
5	24	19.0	19.7	20.3	20.4	19.8	21.2	20.4	20.6	20.4
6	32	19.4	19.0	18.7	18.4	17.1	17.3	18.0	19.3	18.8
7	48	12.3	12.7	12.6	12.9	12.9	12.9	12.6	13.0	12.9
8	56	7.9	8.4	8.4	8.7	8.7	8.7	8.4	7.1	7.7
9	72	3.2	4.6	5.4	5.8	5.9	5.8	4.3	2.8	4.0
10	80	2.1	3.1	3.6	3.9	4.0	3.4	2.4	1.8	2.5
11	32	20.4	21.0	21.8	22.4	22.6	22.7	23.2	22.1	22.1
12	48	16.5	16.6	16.9	17.1	17.1	17.8	17.9	18.0	17.7
13	51	14.7	15.0	15.6	15.2	15.0	15.3	15.5	15.5	15.3
14	56	12.1	12.0	12.5	12.2	12.4	12.6	12.7	12.2	12.3
15	72	8.3	9.1	9.3	9.4	9.3	9.5	9.0	8.0	8.4
16	75	8.7	9.2	9.8	9.8	9.8	9.7	9.4	8.4	9.0
17	80	7.1	7.7	7.6	8.0	7.9	7.7	7.2	5.2	6.5
18	96	3.3	4.5	5.0	4.9	4.7	4.5	3.4	2.4	3.5
19	101	2.7	4.5	5.0	4.7	4.7	4.1	2.6	2.3	3.2
20	104	1.9	2.7	3.6	4.0	4.2	3.9	3.1	2.2	2.9

* Elapsed time after the blocks were removed from the humidity chamber.

† Outside layer refers to the material pared from the four vertical surfaces of the blocks.

evaporation from the surface is greater than the movement of water within the block.

One of the main concerns, however, is whether or not a plaster of paris block centrally located is in contact with soil of about the same moisture content as the average for the whole soil sample. This average moisture content is the value used in a calibration curve. A plaster of paris block in these wire baskets extends into or through all the layers with the exception of nos. 1 and 7.

Since the plaster of paris block is centrally located, layer no. 4, which is the center layer, should most nearly correspond to the moisture content of the soil

in contact with the unit. The ideal condition would be for the moisture content of the soil in contact with the unit to be the same as the average for the entire soil block. In figure 2 the percentage moisture in layer no. 4 is plotted on the ordinate and the average percentage moisture of the entire soil block on the abscissa. The straight line with a slope of 1 represents the ideal relationship. It is apparent that when the soil blocks were put into the humidity chamber they approached this equilibrium, but this was not the case for the blocks which were left under laboratory conditions entirely. This relationship for the soil blocks left under laboratory conditions depends to a large extent upon two factors: first, the nature of the soil, and second, the rate of evaporation from the surface. The nature of the soil affects this relationship in that it determines the rate of

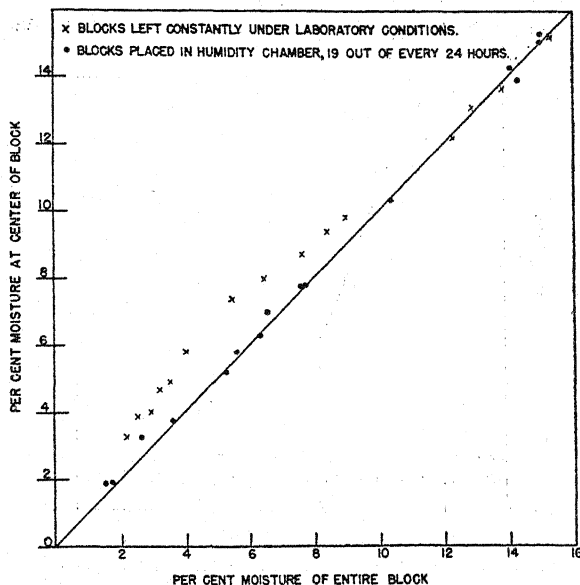


FIG. 2. RELATION OF AVERAGE MOISTURE CONTENT OF ENTIRE SOIL BLOCK TO MOISTURE CONTENT AT CENTER OF BLOCK

movement of water in the soil block. If water movement in the soil is rapid, the calibration curve obtained will approach more closely the correct one, whereas if the water movement is slow, the opposite will occur. If the evaporation from the the surface of the soil block is rapid, the differential in moisture content between the center and outer layers of the block will be accentuated. If evaporation from the surfaces is slow, the calibration curve may approach the correct one. It is this variation in evaporation that is thought to be the cause of failure to obtain duplicate calibration curves when the soil blocks are left under laboratory conditions continuously.

At the time the values presented in table 2 were being obtained without the use of the humidity chamber, calibration curves for the plaster of paris blocks were being concurrently determined for the same soil, by means of the same pro-

cedure. One of these calibration curves, along with a correct one, is given in figure 3. The curve obtained without the use of the humidity chamber is displaced to the left indicating a lower moisture content for the same resistance. This should be the case, since the outer layers are drier than the center, and it is the soil in the center with the higher moisture content which is in contact with the plaster of paris blocks.

Even though the moisture in the soil blocks very closely approached equilibrium after being in the humidity chamber for 19 hours, it is possible that there could be a small error in the calibration curves due to the soil-plaster-of-paris interface. It is essential that this interface present little or no hindrance to the movement of water from the plaster of paris blocks to the soil. For most soils this probably would be true. On very light soils, however, where the pores are relatively large, this might be questioned. It is possible to conceive of a soil in

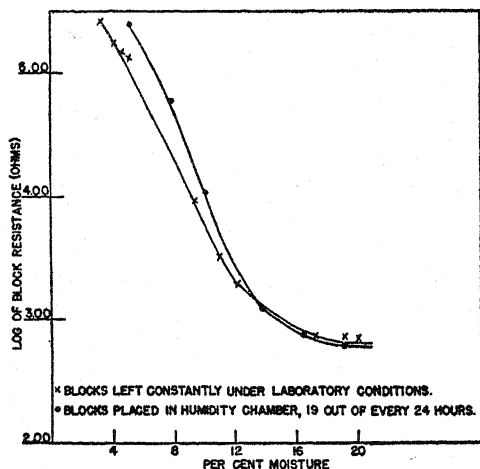


FIG. 3. CALIBRATION CURVES OF CHUALAR LOAM

which the pore space would be of such size that most of the water would be lost at tensions much below that required to remove the water from the plaster of paris blocks. In such a soil the funicles of water would break while there was yet an appreciable amount of water in the plaster of paris block. Under such conditions the water in the plaster of paris would have to be moved by gaseous exchange. Since this process is relatively slow, it would require some time to calibrate such a soil. The calibration curve would probably be correct up to the point where most of the funicles of water in the soil were broken. We have not, however, experienced such a soil in this laboratory.

During the calibration of various soils, tests have been made on a number of samples, varying in texture from very light to medium-heavy, in order to determine whether equilibrium was actually established in all cases. In these tests the soils were left for as long as 187 hours in the humidity chamber. Resistance readings were taken every 24 hours after the first 19-hour period. This was done

at several moisture percentages for each soil. In only one soil, Coachella loamy sand, was there an appreciable change in resistance after 19 hours in the humidity chamber, and this occurred at a very high resistance. The logarithm of the resistance changed from 4.75 to 4.90 during the period from the nineteenth to the forty-third hour. There was no significant change after 43 hours. Coachella loamy sand is a very light soil having 87 per cent sand and a wilting point of about 1.5 to 2.0 per cent moisture. About 90 per cent of the water held in the soil between the "field capacity" and a tension of 15 atmospheres is lost at 1 atmosphere tension. For all practical purposes the change in resistance during the 19- to 43-hour period had no effect on the calibration curve.

Leaving the soil blocks under laboratory conditions for 5 hours and then placing them in a humidity chamber for 19 hours gave satisfactory calibration curves in this experiment. It should be stressed, however, that these lengths of time may not be the most desirable under all conditions. In some cases it may be necessary to either shorten or increase the time of exposure of the soil block to one or the other of the two conditions. The number of points desired for any one calibration will determine the length of time that the block should be allowed to dry under laboratory conditions: the shorter the period of time, the greater the number of points. The length of time the soil block should be left in the humidity chamber can readily be determined by making frequent resistance readings and noting the time at which no further change in resistance occurs. Though in most cases 19 hours should be sufficient, it will probably be necessary for the individual experimenter to vary the time to suit his needs.

The method described in this paper has also been used very satisfactorily for obtaining calibration curves for Shaw-Baver thermal units (4) as well as for the sorption-block method by Davis and Slater (3).

SUMMARY

A method is described for the laboratory calibration of various instruments used in measuring soil moisture *in situ*. The unit being calibrated is surrounded with $\frac{1}{2}$ inch of soil, contained in a wire basket lined with cloth. The soil is wet by capillarity and placed in a humidity chamber to drain. It is then removed and subjected alternately to 5 hours' evaporation under laboratory conditions and 19 hours in a humidity chamber. This procedure is continued until the soil no longer loses moisture when exposed to the air. The weights are recorded and the readings for the various instruments are taken each time the soil is removed from the humidity chamber.

When a wetted block of soil of dimensions $1\frac{1}{2}$ by $2\frac{3}{8}$ by $3\frac{1}{2}$ inches was subjected alternately to 5 hours' evaporation under laboratory conditions and a 19-hour period in a humidity chamber, it was found that there was a small variation in moisture content between the outside layers and the center of the block. This variation had little effect upon the shape or location of the calibration curves.

Evidence is presented to show that when the described procedure is used, the average moisture content of the whole soil block very closely approximates that of the soil immediately surrounding the unit being calibrated.

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POTASSIUM-INDUCED MAGNESIUM DEFICIENCY IN THE MCINTOSH APPLE TREE

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Several workers have suggested that potassium fertilization of apple trees may increase the severity of magnesium-deficiency symptoms or induce magnesium deficiency under some conditions (2, 10, 12, 16, 20). This paper presents confirming data from field and greenhouse studies with McIntosh apple trees and may suggest some of the reasons for this apparent phenomenon.

DESCRIPTION OF MAGNESIUM-DEFICIENCY SYMPTOMS

The visible symptoms of magnesium deficiency of the McIntosh apple tree usually develop after a considerable amount of normal shoot growth has been made. The time of appearance depends, among other things, on the degree of deficiency, the time when vegetative activity started, and the rainfall in the growing season. The greater the deficiency, the earlier the growing season, and the greater the accumulated rainfall in the growing season, the earlier symptoms will appear and the more acute they will be by the time of autumnal leaf fall.

The first evidence of abnormality is usually a fading between the veins of the older leaves on some shoots or spurs. These faded areas commonly turn very pale yellow, but in some instances quickly scorch and brown. Ultimately all affected leaves have necrotic blotches in them. If the necrosis has occurred close to the leaf margin, several blotches may overlap, producing a marginal scorch indistinguishable from that caused by potassium deficiency or toxic spray or fertilizer materials. The leaf injury proceeds from the older leaves on a shoot or spur to the younger ones. On a severely affected branch all of the leaves except a few at the very tips of the shoots may have completely shriveled and abscised by early September. Such loss of effective leaf surface is followed by heavy preharvest fruit drop and by failure of the remaining fruit to mature properly.

If the deficiency is not very acute, visible symptoms may develop on only a single branch or a few branches of a tree. Chemical analysis of the leaves on trees showing slight symptoms is helpful in diagnosis (2, 3, 10, 12, 16, 20). Deficiency symptoms may appear on trees having leaves with magnesium contents of 0.20 per cent dry weight or less if other conditions favor their appearance.

FIELD EXPERIMENTS

All of the field experiments and observations were made at the Burrell Orchards at Peru in the Champlain Valley of New York. All trees have been

¹ The authors acknowledge the assistance of O. C. Compton, F. L. Davis, Jr., and I. Rogel in preparation of the samples for analysis and in performance of some of the analytical work.

growing in sod and have received moderate annual applications of ammonium sulfate fertilizer.

Plot 1

Plot 1 includes four pairs of McIntosh apple trees planted in 1930 on Coloma fine sandy loam. All of the trees showed severe potash-deficiency leaf scorch in 1938. In the spring of 1939, 3 pounds of fertilizer-grade K_2SO_4 was dug into the soil in a narrow band under the tips of the branches of one tree of each pair. The treatment was repeated annually. The other tree of each pair was left as a check. There was marked reduction in the development of leaf scorch on the potash-fertilized trees after two applications, and terminal growth was increased in the third and fourth years of treatment (4). In the fourth year of treatment, 1942, three of the four fertilized trees developed a late-season interveinal leaf blotch similar in appearance to that produced by magnesium deficiency. Table 1 summarizes data obtained in July, 1942, on leaf analysis and appearance of this leaf blotch. The table shows that after 4 years of potash fertilization, potassium was more than twice as high and magnesium was less than half as great in leaves from the three potash-fertilized trees showing the leaf blotch as in the trees paired with them. In the fertilized tree not showing leaf blotch, leaf potassium was lower and leaf magnesium was higher than in the other fertilized trees. Very similar results occurred in 1943. In addition, it was noted that autumn leaf-fall was much earlier on the potash-fertilized trees. On November 7, 1943, the percentages of leaves estimated to have dropped on check and fertilized trees of the four pairs were, respectively: 40 vs. 90, 40 vs. 90, 50 vs. 80, and 40 vs. 90.

Plot 2

Two contiguous rows of McIntosh apple trees planted in 1931 comprise plot 2. One row received annual potash supplements in the 5 years 1938-1942 (see footnote table 2), and the other received none. Though the trees were but a year younger than those of plot 1, only a few showed even slight potassium deficiency scorch in 1938 in contrast with the very serious scorch and stunting of the trees of plot 1 at that time. The potash-fertilized trees recovered completely from the leaf scorch after three treatments. On September 26, 1943, 9 of the 59 trees in the potash-fertilized row had one or more branches on which some basal shoot leaves were showing injuries similar in appearance to magnesium-deficiency leaf blotch, whereas none of the trees in adjacent rows unfertilized with potassium salts showed this injury. Each of the 9 trees showing leaf blotch was paired with a tree similar in size and vigor in an adjacent row to which no potash was added; and a separate sample of 50 leaves was taken from each tree of the 9 pairs on September 26 and 27, 1943. A composite soil sample of eight borings was taken at a depth of 0-8 inches and another at 8-16 inches under each of these trees. Table 2 summarizes leaf and soil analysis data from this plot.

The table shows that 5 years of potash fertilization caused a very marked in-

crease in leaf potassium and in exchangeable potassium in the surface soil, a very significant decrease in leaf magnesium and exchangeable magnesium in the surface soil, some decrease in leaf calcium, and rather variable exchangeable calcium in the surface soil.² A striking increase in exchangeable potassium in the subsurface soil and a decrease in exchangeable magnesium followed potash fertilization.

The means of the subsurface soil analyses indicated higher pH and exchangeable calcium and magnesium and lower exchange capacity and exchangeable potassium than the means of the surface soil analyses. The mean of the exchangeable potassium analyses of the subsurface samples increased from 0.05

TABLE 1

Apparent effects of 4 years of potash fertilization on leaf analysis and symptoms of McIntosh apple trees

PAIR	LOCATION	TREATMENT	1942 LEAF ANALYSIS*			SYMPTOMS†
			Ca	Mg	K	
			<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
1	71-28	+K‡	0.90	0.08	2.40	—Mg blotch
	71-27	Ck§	1.15	0.45	1.01	None
2	72-26	+K	1.01	0.12	2.08	—Mg blotch
	72-27	Ck	1.47	0.26	0.75	—K scorch
3	72-29	+K	0.98	0.19	1.83	None
	72-28	Ck	1.24	0.20	1.16	None
4	73-28	+K	1.10	0.13	1.95	—Mg blotch
	73-26	Ck	1.38	0.42	0.68	—K scorch

* Composite sample of 50 shoot leaves per tree taken in July, 1942. Analysis on a dry-weight basis.

† —Mg blotch is described in the text. —K scorch is a staining and necrosis usually originating close to the margin of the leaf blade.

‡ Starting in 1939, 3 pounds of K_2SO_4 , fertilizer grade, was dug into the ground under tips of branches every spring.

§ No potash supplements.

to 0.26 m.e./100 gm. soil as a result of potash fertilization, and this was accompanied by decreases in exchangeable magnesium and calcium. Mean replaceable Mg and Ca figures were higher, however, in the subsurface soil under the fertilized trees than in the surface soil under the unfertilized trees.

Earlier autumn leaf-drop from potash fertilization, mentioned in the discussion of plot 1, occurred also in plot 2. On November 5, 1943, the 9 potash-fertilized trees of table 2 showed an average leaf-fall of 79 per cent, whereas the

² The leaf samples from plot 2 were taken 2 months later than the leaf samples from plot 1, and they are not directly comparable with the samples from plot 1. This is because potassium, as percentage of dry weight, normally decreases and calcium increases as the season advances, whereas magnesium seems to remain relatively stable (3, 20).

TABLE 2

Apparent effects of 5 years of potash fertilization on analysis of leaves from McIntosh trees and analysis of soil under the trees in 1943

TREATMENT	PAIR	LEAF ANALYSIS*			SOIL† SAMPLED AT 0-8-INCH DEPTH				
		Ca	Mg	K	pH	Exchange capacity	Exchangeable cations		
		per cent	per cent	per cent			Ca	Mg	K
		<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>			<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>
+K‡	1	1.46	0.14	1.44	4.5	7.52	2.95	0.13	0.21
Ck§		1.67	0.34	0.73	5.0	8.51	3.21	0.19	0.04
+K	2	1.19	0.10	1.57	4.7	7.00	1.51	0.10	0.27
Ck		1.42	0.32	0.68	5.0	8.66	4.01	0.20	0.07
+K	3	1.48	0.18	1.17	4.4	7.87	2.08	0.08	0.48
Ck		1.79	0.42	0.53	4.9	9.05	3.53	0.23	0.08
+K	4	1.37	0.13	1.35	4.3	7.57	1.80	0.11	0.23
Ck		1.71	0.35	0.70	4.9	7.83	2.26	0.19	0.07
+K	5	1.25	0.11	1.45	4.5	7.99	2.10	0.11	0.30
Ck		1.81	0.22	0.99	4.7	7.95	2.35	0.19	0.07
+K	6	1.27	0.14	1.17	4.9	8.48	3.84	0.26	0.32
Ck		2.01	0.38	0.67	4.6	6.91	2.33	0.26	0.20
+K	7	1.34	0.11	1.29	4.1	7.46	2.26	0.11	0.40
Ck		1.89	0.31	0.78	4.3	8.62	1.86	0.26	0.10
+K	8	1.27	0.08	1.57	4.3	8.51	2.42	0.15	0.42
Ck		1.68	0.32	0.63	4.4	8.42	1.84	0.24	0.20
+K	9	1.49	0.14	1.24	4.3	8.98	2.68	0.22	0.43
Ck		1.79	0.29	0.74	4.6	8.74	2.72	0.31	0.24
+K Average.....		1.34	0.13	1.36	4.4	7.93	2.40	0.14	0.34
Ck Average.....		1.75	0.33	0.72	4.7	8.30	2.67	0.25	0.12
8-16-inch Depth									
+K Average.....					5.0	5.47	2.98	0.48	0.26
CK Average.....					5.2	5.77	3.31	0.72	0.05

* Composite of 50 shoot leaves from a single tree, sampled at random on September 26 and 27, 1943. Analysis on a dry-weight basis.

† Composite of eight borings from under the branches of a single tree.

‡ Potash amendments as follows: 1938, 5 pounds 60 per cent KCl; 1939, 3 pounds 48 per cent K_2SO_4 ; 1940, 2 pounds KCl; 1941, 3 pounds KCl; 1942, 3 pounds KCl; 1943, no potash fertilizer.

§ No potash supplement.

|| Mean H-ion concentration converted to pH.

corresponding check trees averaged 52 per cent, a heavier leaf-drop having occurred on the potash-fertilized tree of each pair. If these 9 sets of trees, in which the potash-fertilized member had shown blotch, are excluded, the average leaf-fall for the 50 remaining trees of each row was as follows: row 28 (no potash), 46 per cent; row 29 (potash), 72 per cent; row 30 (no potash), 51 per cent.

In 50 of the 59 sets of three trees, the leaf-fall was heavier on the potash-fertilized tree of row 29 than on the corresponding tree of either row 28 or row 30; in 8 sets, the leaf-fall of one tree of either row 28 or row 30 equalled that of the tree in row 29, whereas in 1 set, the leaf-fall of a single check tree exceeded that of the potash-fertilized tree. Thus the influence of low Mg and/or high K in causing earlier autumn leaf-fall, was noticeable, even in the absence of magnesium-deficiency blotch.

TABLE 3

Apparent effects of potash sources and methods of application on leaf analysis of McIntosh apple trees after 3 annual applications

TREATMENT*	1943 LEAF ANALYSIS†		
	Ca	Mg	K
	per cent	per cent	per cent
1. KCl‡ broadcast in 5 foot circle.....	1.12	0.20	1.85
2. K ₂ SO ₄ § broadcast in 5-foot circle.....	1.06	0.16	1.95
3. KCl broadcast in 10-foot circle.....	1.10	0.16	2.09
4. K ₂ SO ₄ spray 1 per cent solution.....	1.18	0.25	1.57
5. No K added.....	1.18	0.35	0.71
6. K ₂ SO ₄ dug in 5-foot circle¶.....	1.10	0.19	1.77
7. KCl dug in 5-foot circle¶.....	1.09	0.19	1.82

* All soil applications were made in April, 1941, 1942, and 1943.

† Average of two composites of 100 leaves taken in July, 1943, from eight experimental trees. Analysis on a dry-weight basis.

‡ KCl was applied at the rate of 2 pounds per tree.

§ K₂SO₄ ground applications at a rate of 3 pounds per tree.

|| 5 sprays were applied during growing season at a rate of 2 gallons per tree.

¶ Treated in 1941 and 1942, but not in 1943.

Plot 3

Plot 3 consists of a small block of McIntosh apple trees planted in 1935 and fertilized differentially with potash salts in a randomized experiment (4). The treatments and 1943 analyses of leaf samples are presented in table 3. In 1942 and again in 1943 potassium-deficiency leaf scorch was eliminated in all of the trees that received potash in any form, though it was present in eight of the nine trees not receiving potash. In 1942, one tree of treatment 1, two trees of treatment 2, and two trees of treatment 3 showed some leaf blotch similar to that produced by magnesium deficiency. In 1943 the only trees showing blotch were the same two of treatment 2. Table 3 shows that the percentage of magnesium in the leaf samples was inversely related to the percentage of potassium. Treatments 2 and 3 produced leaves with the highest potassium and the lowest

magnesium contents. Treatments 4 and 5 produced leaves with the lowest potassium and the highest magnesium contents. Potassium sulfate and potassium chloride appeared to have the same effect on leaf analysis and appearance of leaf blotch.

Plot 4

Plot 4 is situated in a 13 year-old McIntosh orchard that received commercial applications of 60 per cent muriate of potash at a rate of 3 pounds per tree in the spring of 1941, 1942, and 1943. Branches on some of the trees had basal shoot leaves that were showing leaf blotch on September 26, 1943. At that time a composite leaf sample of 50 leaves was taken from each of 16 such trees. In November a soil sample was taken under the branches of each tree, and one was taken in the row middle east of each tree. Every sample was a composite of six to eight borings, and the samples were divided into 0-8 and 8-16-inch depths. Analyses of leaves and soil samples are presented in table 4.

In the leaf samples the magnesium content ranged from 0.08 to 0.20 per cent, and the potassium content from 0.90 to 1.67 per cent. The two samples highest in magnesium were lowest in potassium, and two of the four highest in potassium were lowest in magnesium. But between these extremes there was not a close inverse relationship.³

There was a marked difference between the pH values of the soil samples from under the trees and those of the samples from between the trees. The mean pH of the surface samples under the trees was 4.3, whereas in the row middles it was 5.7. In the subsurface samples, the mean pH under the trees was 4.9 and in the row middles 5.9. Only a small part, if any, of this difference could have been caused by the 3 years of potassium fertilization under the trees. In plot 2 the mean pH was only 0.3 lower under trees fertilized with potash for 5 years than under trees receiving no potash supplement.

The only fertilizers broadcast in the row middles at rates higher than 100 pounds per acre were ground limestone in 1940 at 1,000 pounds per acre and superphosphate in 1939 and 1942 at 300 pounds per acre. These were applied with a centrifugal spreader which broadcast a considerable proportion under the trees as well as between the rows. Thus little, if any, of the pH difference can be attributed to fertilization between the rows.

It seems likely, then, that the use of wettable sulfur sprays and ammonium sulfate fertilizer, both of which are concentrated under the spread of the branches, resulted in this acidification of the soil under the trees.

The difference in pH was accompanied by great differences of exchangeable calcium and magnesium between the surface samples from under the trees and those from the row middles. Mean exchangeable calcium was 0.62 m.e./100 gm. under the trees and 2.97 in the row middles. Mean exchangeable magnesium was 0.06 m.e./100 gm. under the trees and 0.17 in the row middles. With three

³ These samples are not directly comparable with those from plots 1 or 3 because they were taken 2 months later.

TABLE 4

Leaf analysis of some K-fertilized McIntosh trees showing magnesium-deficiency blotch and soil analysis under and adjacent to the trees

LOCATION	LEAF ANALYSIS*			SOIL SAMPLED AT 0-8-INCH-DEPTH†					
	Ca	Mg	K	Position	pH	Exchange capacity	Exchangeable cations		
	per cent	per cent	per cent				Ca	Mg	K
						m.e./100 gm.	m.e./100 gm.	m.e./100 gm.	m.e./100 gm.
59-38	1.16	0.15	1.38	Under‡	4.2	5.97	0.43	0.08	0.31
				Middle§	5.7	5.88	3.24	0.16	0.06
59-41	1.37	0.11	1.33	Under	4.6	5.39	0.91	0.22
				Middle	5.7	5.69	2.61	0.14	0.08
59-46	1.19	0.09	1.67	Under	4.7	5.02	0.97	0.10	0.16
				Middle	5.7	5.51	2.37	0.11	0.05
60-33	1.40	0.13	1.27	Under	4.2	5.11	0.43	0.05	0.12
				Middle	5.6	5.46	2.77	0.17	0.05
60-35	1.42	0.20	0.95	Under	4.2	5.63	0.54	0.02	0.15
				Middle	5.8	5.53	2.91	0.14	0.05
60-36	1.63	0.19	1.18	Under	4.4	5.27	0.40	0.02	0.18
				Middle	5.9	5.79	3.37	0.18	0.07
60-38	1.48	0.08	1.44	Under	4.6	5.63	0.73	0.06
				Middle	5.6	5.67	2.72	0.10	0.07
60-42	1.34	0.17	1.31	Under	4.5	5.09	0.79	0.09	0.08
				Middle	5.7	5.19	2.55	0.14	0.05
60-46	1.64	0.18	1.18	Under	4.4	5.57	0.56	0.05	0.10
				Middle	5.6	5.02	2.28	0.13	0.06
60-47	1.28	0.12	1.47	Under	4.4	5.72	0.48	0.05	0.19
				Middle	5.7	5.44	2.37	0.05
60-51	1.43	0.18	1.09	Under	4.1	5.05	0.47	0.08	0.14
				Middle	5.7	5.79	3.76	0.37	0.17
60-52	1.51	0.17	1.47	Under	4.3	6.41	0.67	0.06	0.22
				Middle	5.8	6.27	4.00	0.34	0.06
61-29	1.44	0.17	1.11	Under	4.1	6.14	0.80	0.08	0.08
				Middle	5.6	5.30	3.84	0.14
61-30	1.60	0.17	1.26	Under	4.1	6.51	0.54	0.04	0.13
				Middle	5.6	5.23	2.85	0.14	0.06

TABLE 4—Continued

LOCATION	LEAF ANALYSIS*			SOIL SAMPLED AT 0-8-INCH-DEPTH†					
	Ca	Mg	K	Position	pH	Exchange capacity	Exchangeable cations		
	per cent	per cent	per cent				Ca	Mg	K
	<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>				<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>
61-34	1.23	0.18	1.31	Under	4.3	6.65	0.60	0.06	0.06
				Middle	5.6	5.67	2.91	0.10	0.08
61-43	1.78	0.20	0.90	Under	4.2	5.70	0.54	0.05	0.08
				Middle	5.6	5.60	2.98	0.13	0.07
Average leaf analysis.....	1.43	0.16	1.27						
0-8-inch depth									
Average under trees.....					4.3	5.68	0.62	0.06	0.15
Average in row middles.....					5.7	5.57	2.97	0.17	0.07
8-16-inch depth									
Average under trees.....					4.9	3.46	1.46	0.18	0.14
Average in row middles.....					5.9	3.39	1.69	0.18	0.03

* 50 leaves per tree sampled September 26-27, 1943. Analysis on a dry-weight basis.

† Composite of six to eight borings.

‡ Under the spread of the branches.

§ The trees are 20 feet apart in rows that are 33 feet apart. The samples in the row middles were taken approximately 16 feet east of the experimental trees in the middle of a row.

|| Mean H-ion concentration converted to pH.

exceptions, exchangeable potassium was greater under the trees than in the row middles. The exchange capacity and the exchangeable bases of both surface soil and subsurface samples from plot 4 were considerably less than in the comparable samples from plot 2.

GREENHOUSE STUDIES

In the spring of 1943, some greenhouse work was done to explore potassium-calcium-magnesium interrelationships as they might influence the appearance of deficiency symptoms on the McIntosh apple tree. One-year-old McIntosh-on-seedling nursery trees were planted on February 17 in 2-gallon crocks filled with washed quartz sand. They were cut back to an inch above the bud, and a single shoot was allowed to develop on each tree. All trees were watered with distilled water until April 5, when 15 groups of 12 trees each were selected so that all groups contained approximately the same range of tree size and appearance. These 15 groups were given different combinations of stock nutrient solutions, similar to those used by Hamner, Lyon, and Hamner (9), made up as shown in table 5.

Each tree was watered with 1 liter of solution once weekly. Once a week distilled water containing 0.5 per cent ferric tartrate was flushed through the crocks. On May 20, magnesium-deficiency blotch and potassium-deficiency scorch were appearing on the basal leaves of some of the trees in certain treatments. The trees were harvested June 7 to 10. Weight and height records were taken and duplicate leaf samples were taken for chemical analysis. The leaf analysis data for twelve of the treatments together with observations on symptoms are recorded in tables 6, 7, and 8. The experiment was concluded before decrease in vegetative growth due to deficiency was evident in any trees except those from treatments 12 and 15, which were definitely stunted.

As the proportion of potassium was decreased and that of calcium was increased with no magnesium added (table 6), leaf potassium decreased, leaf calcium increased, and leaf magnesium increased from 0.10 per cent dry weight in treatment 1 to 0.35 per cent in treatment 12. With one ninth of the nutrient solution

TABLE 5
Stock solutions used in the greenhouse study

STOCK SOLUTION	SALTS	IONIC CONCENTRATION <i>m.e./l.</i>
K	KNO ₃	6.00
	KH ₂ PO ₄	2.25
	K ₂ SO ₄	4.50
Ca	Ca(NO ₃) ₂ ·4 H ₂ O	6.00
	Ca(H ₂ PO ₄) ₂ ·H ₂ O	2.25
	CaSO ₄	4.50
Mg	Mg(NO ₃) ₂ ·6 H ₂ O	6.00
	Mg (H ₂ PO ₄) ₂	2.25
	MgSO ₄ ·7 H ₂ O	4.50

obtained from the magnesium stock solution, low leaf magnesium and the appearance of magnesium-deficiency blotch occurred when potassium was high and calcium was low, whereas when calcium was high and potassium low with the same proportion of magnesium in the nutrient, the leaf magnesium increased by 75 per cent and there was no blotch.

As potassium was decreased and magnesium was increased in the nutrient solution with no calcium added (table 7), the leaf potassium decreased from 3.0 per cent of dry weight to 0.6 per cent, leaf magnesium increased from 0.10 per cent to 0.72 per cent, and leaf calcium increased from 0.5 per cent to 1.5 per cent. With one ninth of the nutrient from the calcium stock solution and with high potassium, leaf calcium was 0.7 per cent. With the same amount of calcium added and with low potassium, leaf calcium was 1.1 per cent.

As calcium was decreased and magnesium was increased in the nutrient solution with no potassium added (table 8), the leaf calcium decreased from 2.0 per

cent dry weight to 1.5 per cent, leaf magnesium increased from 0.35 per cent to 0.72 per cent, but potassium remained relatively stable, decreasing only 0.1 per cent.

TABLE 6

Effects of decreasing potassium and increasing calcium in nutrient on analysis of McIntosh apple leaves

TREATMENT	PROPORTIONS OF STOCK SOLUTION USED IN NUTRIENT SOLUTION-9THS*			LEAF ANALYSIS†			SYMPTOMS‡
	Ca	Mg	K	Ca	Mg	K	
				<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
1	0	0	9	0.5	0.10	3.0	—Mg blotch
3	3	0	6	0.7	0.10	3.0	—Mg blotch
6	6	0	3	1.1	0.15	2.2	—Mg blotch
12	9	0	0	2.0	0.35	0.7	—K scorch
2	1	1	7	0.7	0.16	3.1	—Mg blotch
10	7	1	1	1.5	0.28	1.5	None

* Ca stock solution was full nutrient minus Mg and K

Mg stock solution was full nutrient minus Ca and K

K stock solution was full nutrient minus Mg and Ca

For full details of solution composition see table 5.

† There were 12 trees per treatment. Analysis figures are the averages of analyses of a composite sample from trees 1 to 6 and a composite sample from trees 7 to 12. Leaves were sampled at the end of the experiment about 12 weeks from the beginning of vegetative activity. Analysis on a dry-weight basis.

‡ In most cases the leaf symptoms occurred only on basal shoot leaves and appeared only after 6 to 8 inches of shoot growth had occurred.

TABLE 7

Effects of decreasing potassium and increasing magnesium in nutrient on analysis of McIntosh apple leaves

TREATMENT	PROPORTIONS OF STOCK SOLUTION USED IN NUTRIENT SOLUTION-9THS*			LEAF ANALYSIS†			SYMPTOMS‡
	Ca	Mg	K	Ca	Mg	K	
				<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
1	0	0	9	0.5	0.10	3.0	—Mg blotch
4	0	3	6	0.7	0.22	2.7	None
9	0	6	3	0.9	0.53	1.7	None
15	0	9	0	1.5	0.72	0.6	—K scorch
2	1	1	7	0.7	0.16	3.1	—Mg blotch
11	1	7	1	1.1	0.54	1.3	None

* See footnote * table 5.

† See footnote † table 5.

‡ See footnote ‡ table 5.

These data seem to indicate that the potassium supply in the nutrient medium had a very profound effect on magnesium and calcium levels of apple trees and on the appearance of magnesium-deficiency blotch, whereas the magnesium

supply had only a slight effect on potassium levels of the leaves. The effects of potassium supply on magnesium content of leaves shown in table 6 could not have been caused by changes in ability of the roots to absorb magnesium, because no magnesium was in the nutrient solution, and the effects of potassium supply on calcium content of leaves shown in table 7 could not have been caused by changes in ability of roots to absorb calcium, because no calcium was in the nutrient solution.

GENERAL DISCUSSION

There seems to be no doubt that, under the conditions of these field studies, visible magnesium-deficiency symptoms were induced on McIntosh apple trees as a result of potassium fertilization for 3 or more years. There may be some question as to whether this was due to an effect of potassium on the soil, on the trees, or on both the soil and the trees.

TABLE 8

Effects of increasing magnesium and decreasing calcium in nutrient on analysis of McIntosh apple leaves

TREATMENT	PROPORTIONS OF STOCK SOLUTION USED IN NUTRIENT SOLUTION-9THS*			LEAF ANALYSIS†			SYMPTOMS‡
	Ca	Mg	K	Ca	Mg	K	
				<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
12	9	0	0	2.0	0.35	0.7	-K scorch
13	6	3	0	1.6	0.54	0.7	-K scorch
14	3	6	0	1.5	0.72	0.7	-K scorch
15	0	9	0	1.5	0.72	0.6	-K scorch
10	7	1	1	1.5	0.28	1.5	None
11	1	7	1	1.1	0.54	1.3	None

* See footnote * table 5.

† See footnote † table 5.

‡ See footnote ‡ table 5.

Table 2 presents some data showing changes in soil exchangeable cations that followed several years of potassium fertilization. In both the surface soil and subsurface soil samples, the increase in exchangeable potassium due to fertilization was accompanied by almost proportional decrease in exchangeable magnesium. But there was much more exchangeable magnesium in the subsurface than in the surface soil, and almost twice as much in the subsurface soil under the K-fertilized trees as in the surface soil under the check trees. Previous studies (15) indicated a very satisfactory root penetration at the depth of the subsurface soil samples. Table 4 presents some data on the differences of exchangeable cations in soil samples taken under trees fertilized with KCl for 3 years and in samples taken outside the area so fertilized. Replaceable potassium was materially higher in the fertilized zone under the trees in most cases. Replaceable magnesium of the surface samples was higher in the unfertilized row middles, but there was no difference in the subsurface samples. There was a great deal

more replaceable calcium in the surface soil from the unfertilized area than under the trees. It seems likely that much of the loss of calcium and magnesium under the trees was due to the wettable sulfur spray program and to the annual use of ammonium sulfate. Volk and Peech (19) have reported acidification of Florida citrus soils as a result of sulfur sprays. Batjer and Sudds (1) have reported acidification of the soil under apple trees in West Virginia due to the use of ammonium sulfate. Be that as it may, there was more available magnesium outside the perimeters of the tree tops, and apple tree roots are known to ramify extensively far beyond the spread of the branches. Thus, the effects of potash fertilization on soil exchangeable cations, though significant, involved only a small fraction of the soil mass permeated by the apple tree roots, and it is difficult to attribute the appearance of magnesium-deficiency blotch in these plots to the changes in the soil by themselves.

On the other hand, the greenhouse study (tables 6, 7, 8) together with the data of other workers points convincingly to the conclusion that magnesium deficiency was induced in these plots by the action of potassium in mutual ion replacement or ion competition, effects on the absorption mechanism of the roots or within the trees rather than on the soil. To cite a few instances of supporting literature, Collander (7) studying ion competition in a large number of different plants found that potassium was absorbed more rapidly and in greater quantity than calcium and magnesium. Van Italie (18) in studying the effects of different combinations of cations in the exchange complex of an initially acid soil, on the mineral content of Italian rye grass, found that increasing the replaceable potassium decreased the absorption of magnesium. Loehwing (14) found that addition of KCl to a muck soil growing grain crops caused reduction of the calcium and magnesium contents of the plants. Carolus (5), working with beans in pot culture, found that potassium additions to the nutrient medium markedly decreased magnesium absorption. Thomas and Mack (17) found that potassium fertilization decreased the calcium and magnesium content of corn foliage very markedly. Davidson and Blake (8) found that, with peach trees growing in sand culture, increasing potassium in the nutrient solution while holding calcium constant at either low or moderate levels decreased the amounts of calcium and magnesium in the new shoot growth. Chapman and Brown (6) found that citrus trees receiving 350 to 400 p.p.m. potassium had very high potassium content of leaves and very low calcium content. Hoagland and Chandler (11) and Lilleland and Brown (13) found that, in prune trees, increased absorption of potassium after fertilization of the soil with this element was accompanied by decreased absorption of calcium or magnesium or both.

The general significance under orchard conditions of this effect of potash fertilization in bringing about magnesium deficiency of fruit trees has yet to be determined. Certainly magnesium deficiency is a problem in some orchards that have not been fertilized with potash (2), and there may be enough exchangeable calcium and magnesium in many orchard soils so that magnesium deficiency might not be induced by heavy annual potash fertilization. But it is interesting that the published experimental work on magnesium deficiency and its control in apple orchards of England, New Zealand, Canada, and Massachusetts has

followed a period of 3 or more years during which potassium fertilization has become a rather common practice in those areas. It seems possible, at least, that the problem of magnesium deficiency has been brought about partly as a result of continued potassium fertilization of orchards on soils with low exchange capacities and low exchangeable calcium and magnesium.

Mature apple trees situated on acid soils low in exchange capacity seem to be very slow to recover from magnesium deficiency when soil applications of magnesium salts are made (2, 16). This may be due in part to the fact that exchangeable potassium, though perhaps low in absolute quantity, is likely to be high enough in these magnesium-deficient soils to produce an unfavorable magnesium-potassium relationship at the absorbing surfaces of the roots or within the tree.

Acidification of the soil under apple trees as a result of spraying with wettable sulfurs and the use of ammonium sulfate may also contribute to the appearance of magnesium deficiency under some conditions. Certainly any combination of practices that can cause in a 12 year period a drop in pH of surface soil from 5.7 to 4.3, a decrease of exchangeable calcium from 3.0 to 0.6 m.e./100 gm., and a decrease of exchangeable magnesium from 0.17 to 0.06 m.e./100 gm. surface soil (table 4) could ultimately produce both calcium and magnesium deficiencies of trees with their root systems mostly confined to that soil. The trees in the plots of these experiments were small enough so that there was a strip of 10 to 16 feet between the tips of the branches in the row middles. In most orchards 25 or more years old, however, the tree canopies cover a much larger proportion of the orchard floor, and the spray and fertilizer treatments would affect more soil.

SUMMARY

Magnesium-deficiency leaf blotch was induced in McIntosh apple trees on acid soil low in exchangeable bases as a result of fertilization for 3 or more years with muriate or sulfate of potash. Decrease in leaf magnesium and increase in leaf potassium accompanied the appearance of the symptoms. The orchard studies and accompanying greenhouse studies seemed to indicate that the appearance of magnesium-deficiency leaf blotch resulted primarily from the competitive effect of potassium at the root surface or within the tree. The potash fertilization also caused increased exchangeable potassium and decreased exchangeable magnesium in surface soil under the trees. Twelve years of spraying chiefly with wettable sulfurs, accompanied by annual applications of ammonium sulfate, caused marked acidification of the soil under some trees affected by magnesium-deficiency leaf blotch.

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SOME EFFECTS OF pH ON THE GROWTH OF CITRUS IN SAND AND SOLUTION CULTURES¹

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The pH of a nutrient medium may exert an effect upon plant growth in two general ways: direct and indirect. The direct mechanism is considered as involving some specific action of hydrogen or hydroxyl ions on the physiological activities of the plant, such as, for example, absorption, respiration, or activity of enzymes. Among the indirect effects of pH are those resulting from its influence on the solubility of mineral constituents in the nutrient medium, biological activity, and the physical conditions of the soil.

An enormous amount of work has been reported relative to the effects of pH on plant growth, but little has been done toward separating the direct from the indirect effects. The most recent work along this line is that by Arnon *et al.* (1, 2). These workers grew lettuce, tomatoes, and Bermuda grass in nutrient solutions which ranged from pH 3.0 to 9.0. There was little evidence of any direct effect of either hydrogen or hydroxyl ions upon the plants at pH values between pH 4.0 and 8.0. Plant growth failed completely, however, at pH 3.0, and growth was poor at pH 9.0.

Three experiments covering a range from pH 2.0 to 11.0, carried out to study the effects of pH on the growth of citrus, are reported in the present paper. Various complications entered into each of these experiments, but it has been possible to draw a number of conclusions regarding the direct effects of hydrogen and hydroxyl ions on the growth of citrus. The nature of the complications which arose is also of interest and serves to emphasize some of the complexities involved in this type of study.

EXPERIMENTAL

In undertaking this investigation, it was postulated that if citrus made abundant, healthy growth over a wide range in pH, it would indicate that hydrogen and hydroxyl ions have little *direct* deleterious effect upon the growth of citrus within the limits of that range. The prime objective throughout was, therefore, to establish, the pH limits within which healthy growth could be obtained.

Experiment I

Procedure. This experiment was carried out to study the effect of pH on sweet-orange seedlings in sand cultures under acid conditions. A number of

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3-gallon pots were filled with quartz sand in which finely ground magnetite had been incorporated at the rate of 0.5 per cent, as a source of iron. Three sweet-orange seedlings approximately 2 inches in height were planted in each pot, each unit of three pots being served by a single 135-liter vitrified tile reservoir containing a nutrient solution. The composition of this solution, expressed in milliequivalents per liter, was as follows: Ca, 8.33; Mg, 5.00; K, 1.30; Na, 0.28; NO_3 , 8.33; SO_4 , 6.00; PO_4 , 1.00; Cl, 0.28. Mn and Zn were added at the rate of 0.50 p.p.m. each, and B was added at the rate of 0.25 p.p.m. This solution was circulated periodically through the sand cultures by means of a clock-controlled, compressed-air system, as described by Chapman and Liebig (3, 6). Seven such units were set up, except that magnetite was omitted from the sand of two units, and, instead, 0.5 p.p.m. of Fe, from FeSO_4 , was supplied in the nutrient solution.

The seedlings were planted April 1, 1941, and the nutrient solution was circulated through the pots at approximately 10-day intervals until May 16, 1941. The plants had become established and were growing well by that time; hence differential pH treatments were initiated. The pH of the solution in the seven units was adjusted to the following values with NaOH or H_2SO_4 : No. 26, pH 7.0; No. 27, pH 6.0; No. 28, pH 5.0; No. 29, pH 4.0; Nos. 30 and 31, pH 3.0; and No. 32, pH 2.0. All pH determinations in this and in the subsequent experiments were made on samples of the nutrient solution with a Beckman pH meter. The pH of the solution in each tile was adjusted daily, with occasional exceptions, for 66 days. The solutions were circulated through the pots once daily for 20 days subsequent to May 16, and then for 12 minutes out of every 60 minutes for the remaining 46 days. Circulation of the solution through the sand cultures for a period of 10 to 12 minutes is sufficient to equalize the composition of the nutrient solution throughout the system. Thus any changes in the solution in the sand cultures resulting from such factors as plant growth and respiration are largely obliterated by displacement and admixture with the large volume of solution in the tile reservoir. The three sand cultures of each unit retain about 4.5 liters of nutrient solution, whereas the entire volume involved amounts to about 140 liters.

Results. The plants supplied by tile 32 wilted within 4 hours after the solution was adjusted to pH 2.0, and several days later it was clearly evident that they were dying. The leaves and stems were completely dead within a few weeks, and when the plants were removed it was observed that all the fine roots and a portion of the taproot had rotted. In a side experiment, sweet-orange seedlings were planted in sand cultures and maintained under similar conditions at pH 2.5 for over 5 months. They grew very little and the roots gradually rotted, but it is significant that life persisted, in contrast to the rapid death of plants at pH 2.0.

An unexpected condition developed in the cultures maintained at pH values ranging from pH 3.0 to 6.0. Eleven days after the initiation of the frequent circulation period (12 minutes out of every 60), the new growth on the plants at pH 3.0 and 4.0 became slightly iron-chlorotic, and a few days later some of the new growth in the cultures at pH 5.0 and 6.0 also became chlorotic. Differences in growth gradually became more marked, and 66 days after the differential pH

treatments were started, the size or appearance of the seedlings varied decidedly from one pH value to another (fig. 1). The plants at pH 7.0 and 6.0 were approximately 18 inches high; those at pH 5.0, about 11 inches; and those at pH 4.0 and 3.0, approximately 7 inches. The leaves were normal in size at both pH 7.0 and 6.0, but at pH 7.0 they were dark green, whereas at pH 6.0 they were slightly iron-chlorotic. The plants were very chlorotic at pH 5.0 and 4.0, and also at pH 3.0 in the pots that contained magnetite. Those growing in sand without magnetite at pH 3.0, however, were only slightly chlorotic.

In order to confirm the indications that the chlorosis at pH 3.0, 4.0, 5.0, and 6.0 was related directly to some type of iron deficiency in the leaves, a solution of 0.025 per cent FeSO_4 was injected into several chlorotic leaves by means of Roach wicks, and in 8 to 10 days a portion of each leaf became green. Chlorotic leaves

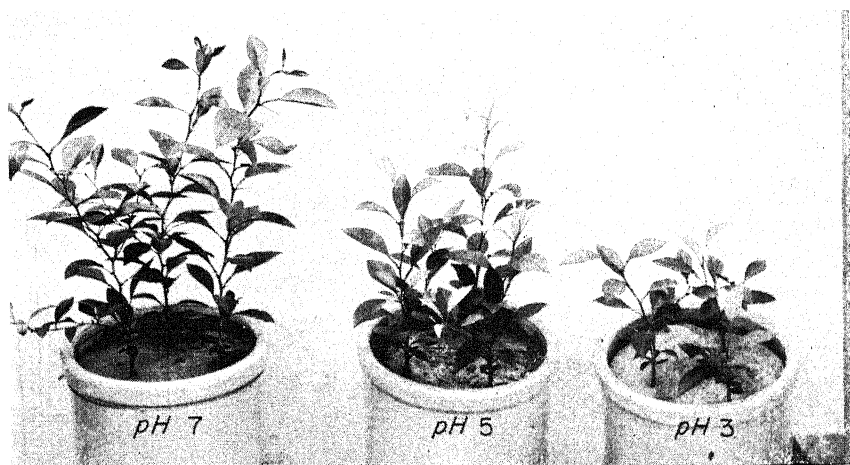


FIG. 1. RELATIVE GROWTH OF SWEET-ORANGE SEEDLINGS IN SAND CULTURES MAINTAINED AT pH 7.0, 5.0, AND 3.0, RESPECTIVELY (EXPERIMENT I)

At pH 7.0, plants were green and healthy; at pH 5.0 and 3.0, iron chlorosis developed. Differential pH treatments were started May 16, 1941; plants were photographed July 21, 1941.

also turned green when the FeSO_4 solution was placed directly upon the upper surface of the blade. It seems certain from these tests that the leaves in all the cultures more acid than pH 7.0 had become deficient in assimilable iron. On the postulate that some heavy-metal impurity in the sand or magnetite, made soluble by the increasing pH, might have been the cause of the disorder noted, spectrographic analyses were made of the solutions from the cultures maintained at pH 7.0, 5.0, and 3.0, with magnetite, and at pH 3.0 without magnetite. The results of these analyses are shown in table 1.

Of the various metals reported, copper and zinc were present in the solutions at pH 5.0 and 3.0 at concentrations which would interfere with good growth of sweet-orange seedlings. It is evident that a portion of both of these impurities came from the magnetite, and it seems certain that iron chlorosis developed

with increasing acidity because of the presence of toxic concentrations of zinc and copper in the nutrient solutions. Chapman, Liebig, and Vanselow (5) showed conclusively in earlier work that slight excesses of zinc, even in the presence of ample soluble iron, would induce iron chlorosis in citrus plants. This effect apparently is associated with an impairment of root activities in which the movement of iron from the roots to the leaves is inhibited.

Because of this unexpected complication, it was recognized that little more could be learned from the experiment concerning the direct effects of pH on plant growth; hence the experiment was discontinued.

TABLE 1
*Spectrographic analysis of culture solutions in experiment I**

ELEMENT	TILE 26	TILE 28	TILE 30	TILE 31
	Sand plus magnetite at pH 7.0	Sand plus magnetite at pH 5.0	Sand plus magnetite at pH 3.0	Sand only at pH 3.0
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Aluminum.....	0.5	0.1	0.2	0.3
Barium.....	0.2	0.2	0.07	0.06
Boron.....	0.3	0.2	0.3	0.3
Chromium.....	<0.004†	<0.004	0.02	<0.004
Cobalt.....	<0.01	<0.01	0.03	<0.01
Copper.....	0.1	0.4	0.6	0.3
Iron.....	0.06	0.14	0.15	0.18
Lead.....	0.015	0.02	0.2	0.25
Manganese.....	0.01	0.7	0.7	0.9
Molybdenum.....	0.01	<0.01	<0.01	<0.01
Nickel.....	<0.01	0.1	0.08	<0.01
Silver.....	0.001	0.001	<0.001	0.001
Strontium.....	0.10	0.18	0.12	0.13
Vanadium.....	<0.1	<0.1	<0.1	0.3
Zinc.....	<0.20	3.0	4.0	2.0

* The writers are indebted to A. P. Vanselow, University of California Citrus Experiment Station, Riverside, California, for this analysis.

† The prefix symbol < means that the element was not detected and hence if present is in an amount smaller than the value given.

Experiment II

In an attempt to avoid the complications that arose in experiment I, a second experiment was set up in solution cultures. In this experiment sweet-orange seedlings were grown in solutions of nearly uniform composition, at reactions which varied from pH 3.0 to 9.0. Despite all efforts to circumvent complications and indirect effects, various difficulties were encountered, and the experiment had to be discontinued before entirely satisfactory conclusions could be reached. The results obtained are of value, however, and in conjunction with experiments I and III contribute certain essential information with regard to direct pH effects.

Procedure. Tiles of 100-liter capacity adapted to solution-culture studies

were used in this experiment. In order to provide a uniform concentration of the various elements at each pH value, the nutrient solution (minus the Fe, Mn, Zn, and B) was first brought to approximately pH 9.3; this caused a portion of certain salts to precipitate. After the precipitate had settled, the supernatant liquid was siphoned off and placed in a series of seven pairs of tiles. The pH of one pair was adjusted to 3.0, that of another to 4.0, and so on at intervals of 1.0 pH unit up to and including pH 9.0. Inorganic iron, manganese, and zinc were added to the solution at pH 3.0, 4.0, 5.0, and 6.0, and humate iron, manganese, and zinc were added at pH 7.0, 8.0, and 9.0. Boron at the rate of 0.5 p.p.m. was added to all the tiles. The pH adjustments were made with NaOH and HNO_3 at frequent enough intervals (daily most of the time) to maintain the variations within the limits of ± 0.2 pH. In order to maintain a uniform sodium concentration in all cultures, whenever NaOH was used to adjust the pH, Na_2SO_4 was added to certain tiles to compensate for the decreased addition of NaOH in the less alkaline cultures. In the acid cultures, where no NaOH was added, all the sodium additions were in the form of Na_2SO_4 . The solutions were changed whenever the concentration reached 10 m.e. sodium per liter. Six sweet-orange seedlings several inches high were set out in each tile on August 15, 1941.

Results. Differences in growth of plants in the various cultures became noticeable within 2 months, and the roots of all the seedlings were somewhat stubby and slightly brown. A few plants were iron-chlorotic even in the acid cultures. Analysis showed that the distilled water used in preparing the solutions contained 0.11 p.p.m. copper, which is sufficient, under certain conditions, to cause root injury to sweet-orange seedlings in solution cultures. In an effort to overcome this possible copper toxicity and get more normal growth, a double-precipitation technique was used from this time on in the preparation of new solutions.

The roots did not show much improvement even after 1 month in these new solutions. The plants at pH 6.0 and 7.0 became severely iron-chlorotic and those at pH 8.0 and 9.0 slightly iron-chlorotic. Iron sulfate or humate iron at the rate of 0.1 p.p.m. Fe was added to each tile three times weekly instead of once a week, but the plants did not respond. Finally, daily additions were made, and within a few weeks some of the chlorotic leaves began to turn green. Subsequently, all the chlorotic leaves on the plants at pH 6.0, and a few at pH 7.0, became green, and new growth at both values was green. Despite the daily additions of humate iron, the plants in the cultures at pH 8.0 and 9.0 remained part iron-chlorotic. Additional efforts were made to find the cause of the stubby root growth in all the cultures, and various changes in technique were tried for a period of almost a year, but without success. It was finally decided that perhaps the purification technique employed had removed some element as yet not proved to be essential, and that it would be useless to continue the pH study under acid solution-culture conditions until the cause of the difficulty could be ascertained. The relative top growth made by the plants in the solutions maintained at values ranging from pH 3.0 to 7.0 from August 15, 1941, to April 23, 1942, is shown in figure 2.

Despite the complications encountered in this experiment, certain inferences can be drawn regarding the effects of hydrogen-ion concentration on the growth

of citrus: The seedlings at pH 3.0 failed to make any observable growth. Their roots gradually rotted, and the leaves turned a bronze color. It would appear from this that the hydrogen ions probably were exerting some direct toxic effect upon the plants. This result agrees with those of Arnon and Johnson (2), who found that lettuce, tomatoes, and Bermuda grass not only failed to grow at pH 3.0, but showed root injury in less than an hour after the plants were transferred to solutions at pH 3.0.

In the present experiment with citrus, excellent green healthy growth of tops took place at pH 4.0 and 5.0, despite the fact that many of the roots were swollen and somewhat brown. It seems certain from these and many subsequent observations that the H ion has little, if any, direct deleterious effect on the growth of sweet-orange plants at pH 4.0. In outdoor solution cultures with bearing

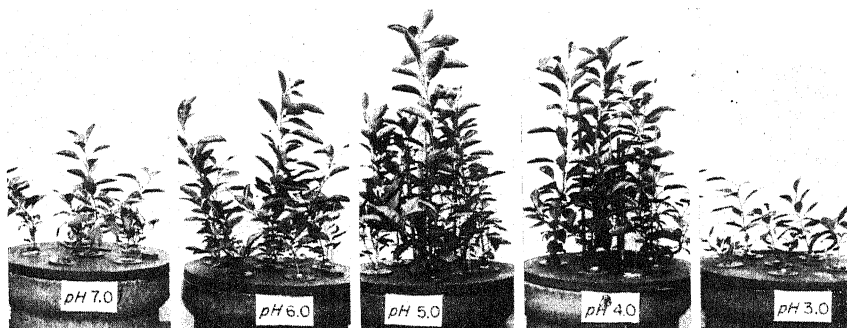


FIG. 2. RELATIVE GROWTH OF SWEET-ORANGE SEEDLINGS IN SOLUTION CULTURES MAINTAINED AT pH VALUES RANGING FROM 3.0 TO 7.0 (EXPERIMENT II)

The plants shown in the culture maintained at pH 3.0 represent the size of the plants at the time differential pH treatments were started (August 15, 1941); these plants, which were entirely healthy and in a growing condition at the time, made no further growth, though they continued to live for many months. Poorer growth at pH 6.0 and 7.0 than at pH 4.0 and 5.0 was associated with iron chlorosis. The top growth at pH 4.0 and 5.0 was healthy, green, and vigorous. Plants were photographed April 23, 1942.

citrus trees, good growth has been obtained consistently at pH values that vary between pH 3.6 and 4.2. There is no indication of root injury in these outdoor trees; in fact, both the roots and the tops are healthy and vigorous. It seems safe to conclude, therefore, that other external conditions being favorable, a hydrogen-ion concentration of pH 4.0 is not noticeably deleterious to the growth of orange trees.

Experiment III

Because of the difficulties encountered in both sand and solution cultures in studying pH effects on the acid side of neutrality, and the need for additional exploratory work before further pH studies were attempted in that range, it was decided to set up experiments to determine, if possible, the maximum alkalinity citrus plants would tolerate. Considerable exploratory work was carried on

before a promising technique was developed. Only the results of the final experiment in this series of tests are given here.

Procedure. This experiment was carried out in sand cultures as in experiment I. Each unit consisted of two 3-gallon pots served by nutrient solution from a single 135-liter tile reservoir. There were five such units. In order to overcome the difficulty brought about by the low solubility of certain essential nutrients at high pH, various nutrient constituents were incorporated into the sand in solid-phase form on the supposition that the plant might obtain ample nutrients by contact exchange or by local root-solid particle solubility independent of the pH of the free solution phase of the system. It had been found earlier by Chapman (4) that the incorporation of sufficient finely ground magnetite in the sand met the iron needs of citrus plants growing in mildly alkaline sand cultures. In the present experiment, finely ground magnetite and bentonite at the rate of 1 per cent each were mixed with quartz sand in the 3-gallon pots. Except for the omission of Na and Cl, the nutrient solution was of the same composition as the solution used in experiment I. Upon repeated circulation through the sand mixture, the solution would gradually come to equilibrium with bases held in exchangeable form in the bentonite, and although it was recognized that the actual amounts of calcium, magnesium, sodium, and potassium in solution and in the solid phase would vary somewhat at different pH values, it was estimated that ample amounts of these elements for growth might be obtained by contact exchange or local root solubility effects.

Three sweet-orange seedlings several inches high were transplanted to each pot on July 22, 1941, and in order to get them well established, they were all grown at a favorable, uniform pH for the first 4 weeks. The pH of the solutions in the five tiles was then changed gradually over a period of another month until it ranged from pH 7.0 to 11.0, at intervals of 1 pH. From September 22, 1941, by which time these differential values had been reached, until the plants were harvested, on February 26, 1942, the solutions were maintained at a daily average pH of 7.0, 8.0, 8.8, and 9.7 in units 9, 10, 11, and 12, respectively. Unit 13 was maintained at pH 11.0 for 8 days. In none of the cultures did the pH vary from these values by more than ± 0.2 pH except at very infrequent intervals. The pH was adjusted with NaOH or H_2SO_4 as required, and the solution was replaced in any unit when the sodium concentration reached approximately 10 m.e. per liter. The nutrient solution was circulated through the pots for 12 minutes during every 60 minutes by means of the control system explained under experiment I (3, 6). In the more alkaline cultures, as might be expected, there was some precipitation of $CaCO_3$ during the course of the experiment, and the sand gradually became impregnated with solid-phase calcium carbonate.

Results. The leaves of the plants in the culture at pH 11.0 wilted within 24 hours after the alkalinity was raised to this point, and all the plants were dead after being maintained for 1 week at this value. The seedlings grew rapidly at pH 7.0, 8.0, and 8.8, and no particular growth differences were apparent for about 3 months. The plants at pH 9.7 also made considerable growth and were green and healthy, but total top growth was not quite so extensive as at the other pH

values (fig. 3). During this 3-month period, substantial growth occurred in all the cultures. The fact that growth was just as good at pH 8.8 as at pH 7.0, and only slightly less at pH 9.7, is regarded as very significant.

During the succeeding 2 months, differences between the plants at pH 7.0, 8.0, and 8.8 began to appear. When the plants were harvested on February 26, 1942, those at pH 7.0 were larger and those at pH 9.8 were smaller than those at pH 8.0 and 8.8, the plants at the last two values being about the same size. Those at pH 9.7 were somewhat bushy, as a result of a branched type of growth

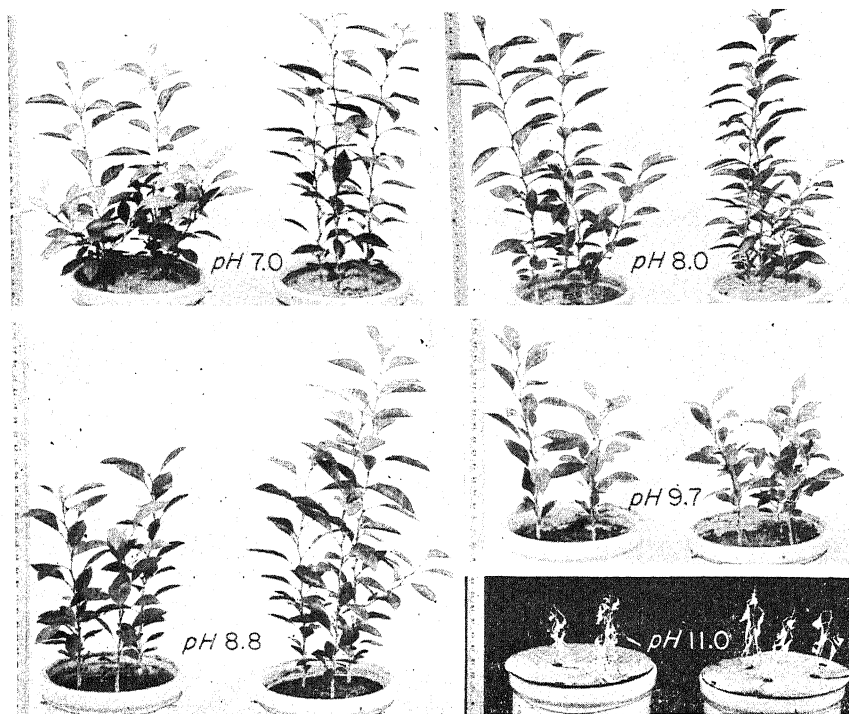


FIG. 3. RELATIVE GROWTH OF SWEET-ORANGE SEEDLINGS IN SAND CULTURES MAINTAINED AT VARIOUS pH VALUES (EXPERIMENT III)

Differential treatments were started September 22, 1941; plants were photographed December 11, 1941. At pH 11.0, the plants died within a few days.

instead of the elongation of a single stem as at the other pH values. The average dry weight per plant (leaves, stems, and roots) was 68.5 gm. at pH 7.0, 47.0 gm. at pH 8.0, 53.8 gm. at pH 8.8, and 17.2 gm. at pH 9.7.

There was a distinct difference in the color and condition of the leaves in the various cultures, also. At pH 7.0, the leaves were a healthy green color; at pH 8.0 and 8.8 the size was normal but many leaves showed a distinct manganese-deficiency pattern; at pH 9.7 the leaves were small to medium and light green to yellow, with necrosis very abundant and typical of injury due to excess sodium. A manganese-deficiency pattern also was pronounced in some leaves at pH 9.7.

At the time of harvest, leaves from plants of all the cultures were analyzed for Ca, Mg, K, Na, N, and P. The resulting data are shown in table 2. The percentage of calcium in the leaves was slightly less at pH 8.8, and decidedly less at pH 9.7, than at pH 8.0 or 7.0. There were no consistent differences in either magnesium or potassium, but sodium increased with each increase in pH, and excess sodium unquestionably was the cause of the leaf necrosis noted in the culture at pH 9.7. The normal sodium content of healthy citrus leaves is less than 0.10 per cent, and it is thought that excess sodium absorption was one of the major factors contributing to the depressed growth at the higher pH values. It will be recalled that during the early months of the experiment, growth was practically identical in the cultures at pH 7.0, 8.0, and 8.8, and only slightly depressed at pH 9.7. It is unfortunate that analyses for sodium were not made at that time. It is believed, however, that sodium gradually accumulated in the plants and thus caused poorer growth in the more alkaline cultures. The nitrogen content of the leaves was not affected significantly by differences in the pH of the solutions, but the percentage of phosphorus was somewhat less at pH

TABLE 2

Certain components of sweet-orange leaves from plants grown in sand cultures at different pH values

CULTURE pH	CONDITION OF LEAVES	LEAF SAMPLE	PERCENTAGE OF DRY MATTER						
			Ash	Ca	Mg	K	Na	N	P
7.0	No necrosis	All leaves	10.64	3.58	0.31	3.11	0.35	3.44	0.14
8.0	No necrosis	All leaves	11.88	3.73	0.34	3.53	0.45	3.60	0.14
8.8	No necrosis	All leaves	10.59	3.16	0.39	3.70	0.53	3.41	0.094
9.7	Many leaves	Nonnecrotic	9.59	2.13	0.29	3.35	0.87	3.17	0.073
	necrotic	Necrotic	13.22	3.06	0.23	3.48	1.63

8.8 than at pH 7.0 or 8.0, and at pH 9.7 the value of 0.073 per cent total phosphorus is in the deficiency range for citrus.

The fact that growth was almost identical in the cultures at pH 7.0, 8.0, and 8.8 during the first 3 months strongly indicates that the subsequent poorer growth at pH 8.0 and 8.8 was due, not to any direct toxic effect of hydroxyl ions, but rather to increased sodium accumulation, manganese deficiency, and perhaps incipient phosphorus deficiency. The early green healthy growth at pH 9.7 also suggests that hydroxyl ions at this concentration are not toxic to citrus. At pH 11.0, however, almost immediate wilting and rapid death occurred, which indicates that this concentration of OH ions exerts a direct, toxic effect upon sweet-orange seedlings.

DISCUSSION

The results of the three experiments reported emphasize the importance of the indirect effects of pH on plant growth and the difficulty of overcoming these so that direct effects may be shown clearly. The indirect effects manifested them-

selves in various ways in these experiments, depending upon the experimental setup. In the first experiment, poor growth of citrus under acid conditions resulted from excessive solubility of zinc and copper brought into solution from impurities in the sand and magnetite. In the second experiment, good growth was obtained at pH 4.0 and 5.0, but growth was progressively poorer at pH 7.0 and beyond, probably because of iron unavailability. In the third experiment, poor growth under alkaline conditions resulted in part from increased sodium absorption and from manganese and phosphorus deficiency. At pH 2.0 and 11.0, the plants were affected almost at once and were killed in a few days. At pH 2.5 and 3.0, they were able to live but made little or no growth. Good growth was obtained at pH 4.0, and in subsequent work sweet-orange trees growing for long periods in solution cultures out of doors made excellent root and top growth when the acidity of the solution was maintained at values which ranged from pH 3.6 to 4.2. Under alkaline conditions, citrus seedlings made healthy, rapid growth for 3 months at pH values from 8.6 to 9.0, and the plants were green and healthy even at pH 9.7 to 10.2. The rate of growth was less at the latter values.

The combined results of the experiments warrant certain general conclusions regarding the direct effects of hydrogen and hydroxyl ions upon the growth of citrus. It seems safe to assert that if nutrient and other environmental conditions are favorable, a concentration of hydrogen and hydroxyl ions corresponding to values extending from somewhat below pH 4.0 to somewhat above pH 9.0 exert no appreciable *direct* ill effect on the growth of sweet-orange seedlings. On the other hand, rapid death occurs at pH 2.0 and 11.0, and it seems certain that at these concentrations hydrogen and hydroxyl ions exert a direct lethal effect.

SUMMARY

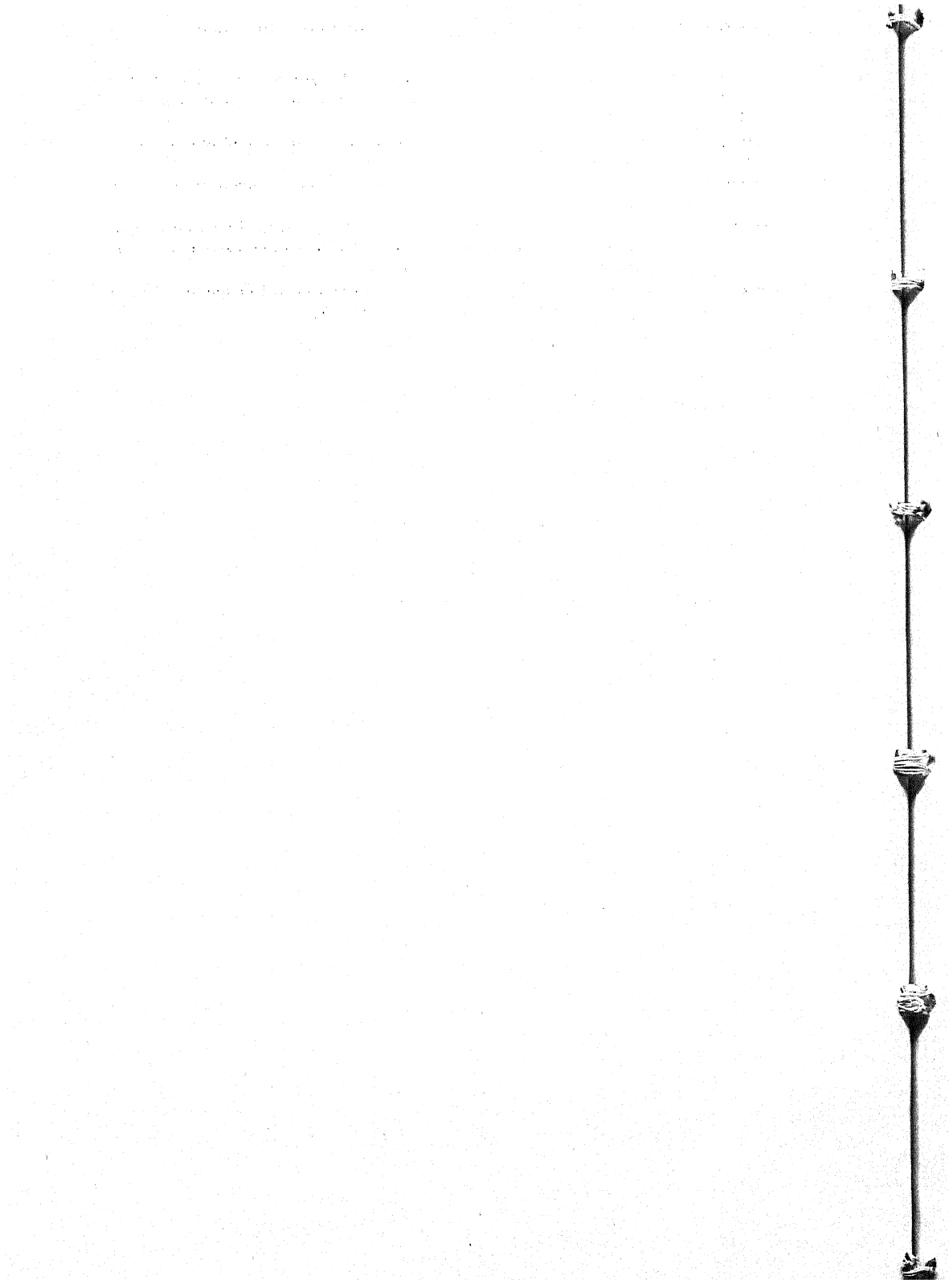
An investigation was undertaken to study the effects of pH on the growth of citrus, with special reference to the direct effects as contrasted with the well-recognized indirect effects.

Three separate culture experiments are reported: two in sand and one in solution, under conditions which ranged from pH 2.0 to 11.0. At these extremes, citrus plants were killed in a few days. At pH 2.5 and 3.0, plant life persisted for months, but little or no growth occurred. Good growth was obtained between pH 4.0 and pH 9.7, though difficulties due to indirect effects were encountered and the actual limits at which hydrogen and hydroxyl ions begin to exert direct deleterious effects were consequently not established. Despite these complications, the results warrant the conclusion that hydrogen and hydroxyl-ion concentrations corresponding to pH values ranging from slightly below pH 4.0 to somewhat above pH 9.0 exert no appreciable *direct* ill effect on the growth of sweet-orange plants.

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THE BACTERIOSTATIC ACTION OF ROSE BENGAL IN MEDIA USED FOR PLATE COUNTS OF SOIL FUNGI

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The enumeration of fungi in the soil by means of plate counts has never been a very satisfactory determination. The fungi, occurring in much smaller numbers than the bacteria and actinomyces, would be crowded on the plates and an accurate counting of their colonies would be impossible unless some means were used to hold down the development of the colonies of the more numerous organisms. The usual method of doing this is by acidification of the plating medium (1, 4, 5, 8). This has served well to eliminate most of the actinomyces and bacteria on the plates, but it did not prevent the spreading of certain fungi. Sometimes when the spreading types were especially abundant, it was impossible to make anything like an accurate count. Ludwig and Henry (4, p. 349) note, "Once this fungus [*Trichoderma*] appeared it became difficult to study other genera, since the plates were rapidly overgrown by it." Other investigators have had similar experiences. Usually, with untreated soil, only once in a while will a plate be so overrun by fungi that it has to be discarded.

Recently Tyner (7) asserted that boric acid effectively suppressed the growth of bacteria and permitted satisfactory counts of fungi in composted soil. He maintained that these counts were very much higher than when sulfuric acid was used as an inhibiting agent.

It is the purpose of this paper to show that higher and more uniform counts of soil fungi may be obtained by using rose bengal instead of acidifying agents in the plating medium and that, in the presence of the dye, spreading of the fungi is reduced to a minimum.

THE INHIBITING ACTION OF ROSE BENGAL

After the partial sterilization of soil by chloropicrin (6), *Trichoderma* developed so markedly that means were sought of inhibiting its growth on plates made for counts of bacteria and actinomyces. Among the materials tested, rose bengal seemed to be promising.² At a concentration of 1 part in 15,000 it entirely prevented the growth of actinomyces and most of the bacteria and kept the *Trichoderma* and other genera of fungi from spreading. In consequence, the individual colonies could be counted. The medium in which the rose bengal was used was

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glucose nitrate soil extract agar (5). A few platings using Waksman's medium (8) with rose bengal instead of acid were made, and these results also were promising. Further tests, however, could not be made at that time.

In plating out soil that had been treated with various materials designed to reduce soil-borne diseases, the spreading of *Trichoderma* on the acidified medium interfered with the accurate counts of fungus colonies. Consequently, platings were made to see whether rose bengal would give as high counts as the acidified medium and whether the conditions of the plates would be improved. The results of the counts are given in table 1. In general, rose bengal in a near-neutral medium allows more colonies to develop than does the pH of 4.2. In

TABLE 1

Comparison of colony counts of fungi obtained with usual acidified media and with near-neutral media to which rose bengal had been added

Fungi in thousands per gram of soil

SOIL SAMPLE	COLONY COUNTS OF FUNGI					
	Glucose nitrate soil extract agar*			Waksman's medium†		
	Acid	Rose bengal		Acid	Rose bengal	
	pH 4.2	1-10,000	1-15,000	pH 4.2	1-10,000	1-15,000
D4	110	...	190	170	...	180
D5	50	...	60	50	...	45
FC	60	150	175	105	110	165
FCy	6	21	23	9	20	25

* Formula: glucose, 10 gm.; NaNO_3 , 1 gm.; K_2HPO_4 , 1 gm.; agar, 15 gm.; soil extract, 1000 ml. (the soil extract was prepared by autoclaving 500 gm. of a good field soil in 1,200 ml. water for 1 hour and filtering through paper; final volume 1 liter). Reaction, pH 6.8 to 7.0.

† Formula: glucose, 10 gm.; peptone, 5 gm.; KH_2PO_4 , 1 gm.; MgSO_4 , 0.5 gm.; distilled water, 1000 ml.; agar, 25 to 30 gm. Enough normal sulfuric or phosphoric acid is added to bring the pH to 3.6 to 3.8; final reaction after sterilization, pH 4.0. In the present work, enough of a mixture of sulfuric and hydrochloric acids to bring the reaction to pH 4.2 was added to bottles of the melted agar just before the plates were poured. This avoided using the higher percentages of agar which its hydrolysis during sterilization would have necessitated.

two of the soil samples the difference is not so striking as in the other two. It has been realized for some time that not all fungi will grow in a medium as acid as that used (1). Waksman (9, p. 18) pointed out that "the majority of fungi can stand greater degrees of acidity than the bacteria and actinomyces." Apparently a great deal depends upon the nature of the fungus flora and upon the buffering capacity of the medium. For instance, Waksman's medium, which contains 0.5 per cent peptone as well as phosphate, gives a higher count at pH 4.2 than does the very slightly buffered glucose nitrate soil extract agar. But at near neutrality (pH 6.8), with rose bengal at 1 to 15,000, the opposite holds true. The differences here, however, are slight and might not hold in a larger series.

One point not shown in table 1 that aids in the routine of making the counts is the virtual absence of bacteria on plates made with glucose nitrate soil extract agar. After 4 days' incubation at 28 C., the colonies of fungi are easily counted, usually without recourse to a microscope, whereas with the medium containing peptone, a greater number of bacteria grow and the fungal colonies have a tendency to spread. If the concentration of the dye is increased, this difficulty can be reduced, but, as can be seen in table 1, a corresponding decrease in the number of fungi also occurs.

Additional tests were made to determine whether the amount of the dye in the medium could be reduced. At a concentration of 1 to 25,000 in glucose nitrate soil extract agar, the average count on six samples was 59,000, whereas with the dye at 1 to 15,000 the average was 60,000. In the former case, however, the condition of the plates was not so good, i.e., there were more bacteria and less inhibition of the spreading fungal colonies. As a counterpart, a medium of the same composition but with tap water replacing the soil extract, was also used to plate out the six samples. The average counts were 54,000 (dye 1 part in 25,000) and 49,000 (dye 1 in 15,000). Soil extract in the medium gives a higher count and also reduces the toxicity of the dye for the fungi. This was also brought out in another experiment wherein ammonium nitrate was substituted for the sodium nitrate in the tap water medium. Using 1 part of the dye in 15,000, counts on samples D4 and D5 were 170,000 and 40,000 respectively, whereas with the glucose nitrate soil extract medium they were 190,000 and 60,000 respectively (table 1). Although these differences are not large, they were found to be quite consistent in other miscellaneous trials.

In addition to these media Czapek's agar (9, p. 226) was used with three modifications: acidified to pH 4.2; with rose bengal 1 to 10,000; and with rose bengal 1 to 15,000. The counts for soil FC were 70,000, 130,000, and 160,000 respectively; for soil FCy, 8,000, 16,000, and 17,000 (compare with table 1). For the most part these figures are somewhat lower than those obtained with the other two media. They bring out the fact that acidification of the plating medium to pH 4.2 reduces the counts perceptibly (1, p. 65).

COMPARISON OF ROSE BENGAL WITH BORIC ACID

As the foregoing tests were being completed, the report by Tyner (7) appeared in which it was shown that boric acid "effectively suppressed the growth of bacteria but permitted a satisfactory count of fungi." A potato-dextrose agar and Lipman and Brown's synthetic agar (3) were used. The latter is similar to Waksman's medium used above except that it contains only 0.05 gm. peptone per liter instead of 5 gm. Boric acid, therefore, seemed very promising as a competitor of rose bengal.

The soil samples plated, the media used, and the counts obtained are given in table 2. Soils of diverse character were deliberately chosen for plating. Number 6A was an unlimed field soil (clay loam); 10B was the same as 6A except it had been limed; GH47 was a sandy loam to which composted soil had been added and the mixture used in a greenhouse bench; W1 was a sandy loam under

a hardwood forest; W2 was taken only 50 yards from W1 but under a pine forest. Rose bengal was added in both cases to make a concentration of 1 part in 15,000, and the pH was adjusted to 6.8.

The results are very striking. Boric acid greatly reduced the counts in all cases, and in the W2 soil rendered the plates virtually sterile. This would seem to mean that the flora in the woods soil is different from that in the field soils (6A and 10B). In any case boric acid is not a satisfactory agent from the point of view of either the counts or the condition of the plates. Rose bengal added to the same base medium (Lipman and Brown's) gave counts comparable with those obtained on glucose nitrate soil extract agar with the dye, although they were somewhat lower in three of the five tests.

Eastwood (2) reported that anisic acid, benzoic acid, and, to a less extent, chrysoidine Y had selective bacteriostatic action. Two of these (benzoic acid

TABLE 2

Counts of fungi obtained on glucose nitrate soil extract agar with rose bengal compared with those obtained on Lipman and Brown's medium modified with rose bengal and with two concentrations of boric acid

Fungi in thousands per gram of soil

Soil Sample	COUNTS OF FUNGI			
	Glucose nitrate soil extract agar	Lipman and Brown's Medium		
	Rose bengal 1-15,000	Rose bengal 1-15,000	Boric acid 0.1 per cent	Boric acid 0.3 per cent
6A	265	310	160	90
10B	210	210	130	35
GH47	200	170	40	15
W1	200	155	20	10
W2	225	195	0.2	0.2

and chrysoidine Y) were added to separate portions of the glucose nitrate soil extract agar and to Waksman's medium at the concentrations recommended, and plates were poured from dilutions of the greenhouse soil and the W2 soil. Benzoic acid and chrysoidine Y proved very unsatisfactory, allowing bacteria to develop and the fungi to spread. The condition of the plates containing Waksman's medium was especially bad in this respect, indicating little toxicity of the materials.

SUMMARY

Acid media commonly used in making plate counts of soil fungi were compared with media of the same composition, except that the reaction was near neutral and rose bengal was added to make a concentration of 1 part in 15,000.

Glucose nitrate soil extract agar containing rose bengal was the best medium found. It eliminated all the actinomyces and most of the bacteria and reduced the spreading of fungal colonies to a minimum. The comparatively few bacteria

that were tolerant of the dye produced soft, raised, glistening colonies that would not be confused with the fungal colonies.

At pH 4.2 the numbers of fungal colonies were reduced on all media when compared with the same media at pH 6.8 and containing rose bengal.

Other inhibiting substances, such as boric acid, benzoic acid, and chrysoidine Y, were entirely unsatisfactory. Rose bengal, 1 part in 10,000, was too toxic and reduced the counts of fungi somewhat. At a concentration of 1 part in 25,000 more bacteria developed on the plates than when 1 part in 15,000 was used, and there was a tendency of the fungi to spread.

Media containing peptone, such as Waksman's plating medium for fungi, or Lipman and Brown's synthetic agar, may be used with rose bengal (1 part in 15,000) for making plate counts of soil fungi. At least twice as many bacteria will develop on these media as on the glucose nitrate soil extract agar, but the counts of fungi will not be very different, although they are usually higher and better differentiated on the latter medium.

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QUALITATIVE STUDIES OF SOIL MICROORGANISMS: VI. INFLUENCE OF SEASON AND TREATMENT ON INCIDENCE OF NUTRITIONAL GROUPS OF BACTERIA¹

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Recent publications from this laboratory (4, 6) have drawn attention to the nutritional requirements of soil bacteria developing on a nonselective medium (soil extract agar). On the basis of these studies a classification was proposed in which these bacteria were grouped according to their nutritional needs. In addition, it was emphasized that the organisms representing these groups were in equilibrium with one another, an equilibrium which seasonal change and soil treatment might disturb. Some results of studies on the influence of these two factors on the incidence of certain bacterial nutritional groups in soil are reported herein.

FIELD PLOT STUDIES

Soil samples were taken periodically (usually at monthly intervals) at a depth of 2 to 6 inches from two plots of different manurial treatment: N—no fertilizer; X—farmyard manure. The plating medium and analytical procedures employed are described elsewhere (3, 5, 6).

The results obtained over a period of 21 months are presented in figure 1 and represent the bacterial response to the combined effects of season, crop, and soil treatment. Organisms with very simple food requirements (group A, those growing well in mineral-glucose medium) were very prominent in the fall and winter of 1940, declined in the summer of 1941, and tended to rise again (though not to the same heights as in 1940) in the following fall and winter, whereas bacteria which require yeast extract (group E) varied more or less conversely. Bacteria requiring known amino acids (groups B and C) or growth factors (group D) showed some fluctuation but none which could be correlated with change of season. On the other hand, organisms growing only in soil extract semisolid agar (group F)³ fluctuated fairly regularly with the season, being low in the late fall and winter and high in the early spring and summer.

It appears that group F is more sensitive to seasonal changes than the other groups but is not appreciably affected by soil treatment or the nature of the crop. Groups B, C, and D do not seem to be significantly affected by any of

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² The authors wish to express their thanks to A. G. Lochhead, Dominion agricultural bacteriologist, for suggesting this problem and for his sustained interest throughout the course of this work.

³ This group of bacteria was originally included in group E by West and Lochhead (6) and is roughly comparable to groups VI and VII of Lochhead and Chase (4).

the factors involved. The variations of groups A and E, however, point to the influence of at least two factors—season and crop. Timothy, grown in 1940, may have stimulated bacteria of group A or depressed those of group E,

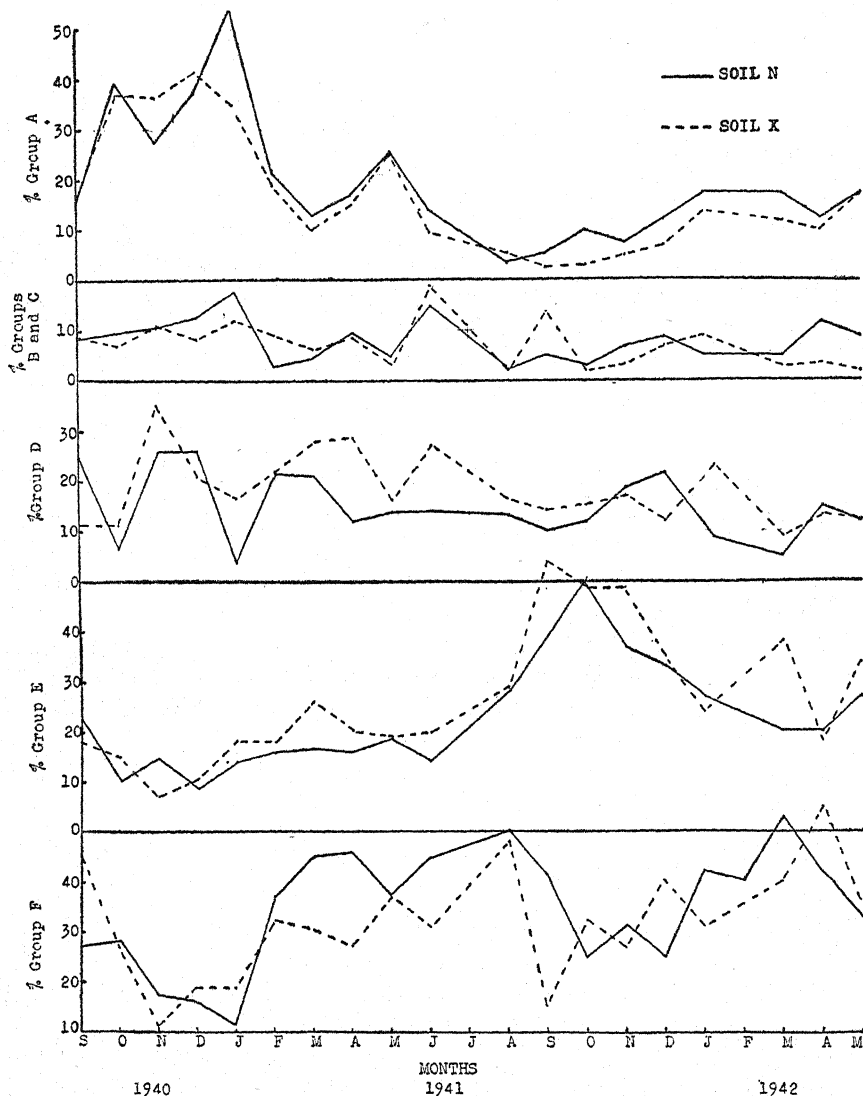


FIG. 1. INFLUENCE OF SEASON ON INCIDENCE OF CERTAIN BACTERIAL NUTRITIONAL GROUPS IN SOIL

whereas mangels, planted in 1941, may have induced an opposite response, resulting in an increase of group E or a decrease of group A. Taylor and Lochhead (5), working with the same soils, obtained "increased counts of Gram-positive and Gram-variable short rods and *Bacterium globiforme*" after mangels

as compared with numbers following timothy. Thus it is quite possible that the nature of the crop exerts an influence as profound as, if not more profound than, the effect of season on specific groups of soil microorganisms.

Further analysis of figure 1 shows that though soil treatment did not influence significantly the seasonal fluctuations of the various groups, it did govern their abundance. Soil X—receiving manure—supported, more or less consistently, larger numbers of bacteria requiring specific growth factors or yeast extract (groups D and E respectively), and soil N—untreated—, larger numbers of bacteria with very simple nutritional needs (group A). Lochhead and Chase

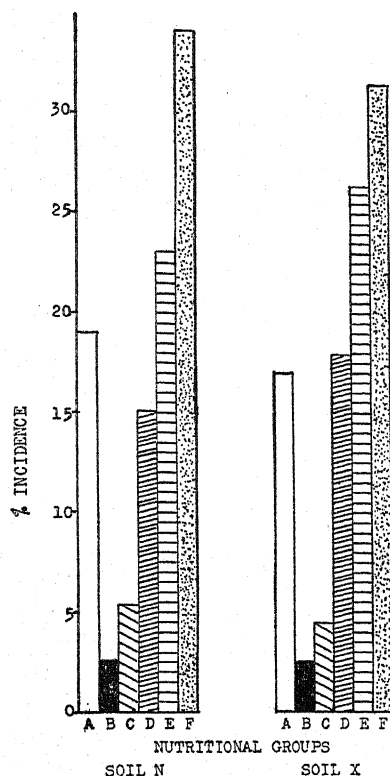


FIG. 2. RELATIVE INCIDENCE OF BACTERIAL NUTRITIONAL GROUPS IN SOIL

(4) working with the same plots also noted that soil X was more favorable to group E and less favorable to group A than soil N. The results with group D are not comparable, as the constituents of the growth-factor medium used were not identical in the two experiments.

Despite the differences noted, the average relative incidence of the nutritional groups over the entire sampling period was found to be remarkably similar in both soils. As may be seen in figure 2, organisms of group F were the most numerous, closely followed by those of group E; groups A and D were next in abundance, and B and C last. This suggests that the bacterial equilibrium

in these two soils has not been changed appreciably by treatment. Taylor and Lochhead (5) also point out that "in a soil of a given type the bacterial flora may be fairly resistant to change even though the productivity may vary as much as ten-fold."

POT EXPERIMENTS

According to the work of West and Hildebrand (1, 7), treatment of soil with red clover, manure, soybeans, carbohydrates, and acetic acid caused an appreciable shift in the bacterial equilibrium of the soil as indicated by their measure of this equilibrium—the bacterial balance index (6). For example, the addition of soybeans, carbohydrates, and acetic acid induced a high bacterial balance index, which means that a relative increase of organisms requiring known amino acids and growth factors and a decrease of bacteria with very simple nutritional needs occurred. This shift in equilibrium was found to be associated with a decrease in severity of strawberry root rot in their soil. The experiments reported below were designed to yield further information concerning the effect of different soil amendments on the equilibrium between the bacterial nutritional groups in the soil, particularly with a view of inducing a high bacterial balance index.

Strawberry root rot soil from St. Catharines, Ontario, received the following treatments:

SERIES	TREATMENT	SERIES	TREATMENT
Control soil	None	E	1% dextrose
A	3% green strawberry plants	F	5% dextrose
B	5% green soybean plants	G	5% soluble starch
C	5% green red clover plants	H	5% molasses
D	5% ground filter paper	I	Acetic acid to pH 4.5

These treatments were applied to the soil at 60 per cent of its moisture-holding capacity, thoroughly mixed, and the mixtures placed in $\frac{1}{4}$ -gallon crocks in duplicate; the crocks were covered, weighed, and maintained at room temperature (20–25°C.). Water was added periodically to compensate for loss by evaporation. Samples for analysis were removed at suitable intervals; the analytical procedures employed were the same as in the field plot studies.

Influence of treatment on the relative incidence of bacterial nutritional groups

Although samples were taken at three periods—40, 120, and 360 days—the data for only the first and last are summarized in table 1, the results of the second being intermediate. After 40 days group A was lower in soils treated with molasses, starch, 5 per cent dextrose, and especially cellulose than in the control soil. With time, this group declined in abundance in all soils except the molasses-treated, which remained virtually unchanged, and the cellulose-treated, in which the group became particularly prominent. In general, after 360 days, the percentage incidence of these bacteria was somewhat greater in the treated soils than in the control.

Bacteria requiring amino acids were markedly stimulated by cellulose and soluble starch. Soybeans, dextrose, starch, and acetic acid were also favorable, a fact which explains, in part, the higher bacterial balance index in these soils than in the control. After 360 days the effect was still noticeable in soils treated with soybeans and dextrose. Red clover also induced an increase of these organisms at this time.

Organisms with specific growth factor requirements were only moderately stimulated by the treatments. At the end of the experimental period, however, certain of the amendments such as soybeans and cellulose seemed actually to depress the group.

TABLE 1

Influence of soil amendments on the incidence of certain bacterial nutritional groups

SOIL TREATMENT	GROUP A, GROWING WELL IN MINERAL- GLUCOSE MEDIUM		GROUPS B & C, REQUIRING AMINO ACIDS		GROUP D, REQUIRING KNOWN GROWTH FACTORS		GROUP E, REQUIRING YEAST EXTRACT		GROUP F, GROWING IN SOIL EXTRACT SEMISOLID AGAR ONLY		BACTERIAL BALANCE INDEX	
	40 days	360 days	40 days	360 days	40 days	360 days	40 days	360 days	40 days	360 days	40 days	360 days
	%	%	%	%	%	%	%	%	%	%		
Control soil.....	37	7	8	8	18	23	12	46	25	13	-4	+29
3% Strawberry tis- sue.....	50	17	8	8	27	18	9	26	6	31	-17	+18
5% Soybean tissue..	37	28	15	14	31	8	8	42	9	8	+17	+11
5% Red clover tis- sue.....	38	6	9	19	26	16	18	40	9	19	-2	+32
5% Cellulose.....	6	63	48	9	20	4	12	20	14	4	+51	-56
1% Dextrose.....	41	26	4	16	22	11	4	29	29	18	-25	+15
5% Dextrose.....	22	14	16	15	25	26	37	31	5	14	+7	+29
5% Soluble starch...	16	13	28	7	21	23	30	44	5	13	+26	+10
Molasses.....	12	15	17	3	36	18	25	40	10	24	+23	+23
Acetic acid to pH 4.5.....	29	9	17	5	32	14	20	42	2	29	+22	+12

After 40 days' incubation, group E was higher in soils with red clover, 5 per cent dextrose, starch, molasses, and acetic acid than in the control. There was a tendency for this group to increase with time, until at 360 days 40 per cent of the isolates belonged to it in six of the soils including the control. Certain treatments such as cellulose again appeared to repress these bacteria.

Group F was depressed by most of the treatments at 40 days. After 360 days, however, it was more abundant than in the control in soils receiving strawberry tissue, molasses, and acetic acid. Once more, cellulose seemed to exert an inhibitory effect.

The foregoing analysis of the data in table 1 shows how extensively certain treatments can modify the incidence of some bacterial nutritional groups in soil and how the latter may vary even in untreated soil, a phenomenon which was recorded previously (2). On the basis of these results, it is difficult to

generalize as to the effect of broad types of substances as proteinaceous materials or carbohydrates on the groups of bacteria studied. For example, the two legumes, both comparatively rich in nitrogen, produce different initial and residual effects, as do the various carbohydrates used. The quantity of the treatment may also induce a different response (compare 1 and 5 per cent dextrose).

Bacterial balance index

The influence of various amendments on the bacterial nutritional groups in soil is brought out very clearly by the bacterial balance index of West and Lochhead (6). The results after 40 days (table 1), on the whole, corroborate those of West and Hildebrand (1, 7) who found that soybeans, dextrose, and acetic acid increased the "B.B.I." of root-rot soil, whereas red clover was comparatively ineffective. The data obtained in the present work indicate that other carbohydrates (starch, cellulose, and molasses) also increased the index. On the other hand, strawberry tissue lowered it. Since this material is incorporated in soil under ordinary farming practices, it may be one of the factors responsible for the shift of the bacterial equilibrium in soil to a point where it becomes unfavorable to the plant, and a root-rot condition develops (1, 7). Again, the quantity of material used appears to exert a very important effect: 1 per cent dextrose actually depressed the index to -25 , whereas 5 per cent increased it to $+7$. Larger quantities may well raise the index farther (7). Residual effects of treatments must also be considered, as is borne out by the results with cellulose: after 40 days this material gave an index of $+51$, but after 360 days the equilibrium had shifted to an extremely low level of -56 . The tendency for the "B.B.I." of the control soil to increase with time was observed previously (2) and may reflect a natural tendency of normal soil which has been removed from the field, dried, remoistened, and incubated at room temperature to reach an equilibrium with its new environment.

DISCUSSION

In a given soil environment, the components of the microbial population are in equilibrium with one another. Any change in this environment produced by season, growing crop, or soil treatment may shift this balance to a new one which is a reflection of the biological activity of the new factor. This applies to the interrelationships not only among broad groups of microorganisms such as protozoa, fungi, or bacteria but also among the constituent members of these groups. To what extent the new equilibrium will persist depends on the quantitative and qualitative intensity of the new environmental factor and the length of time over which it operates, because it is obvious that the inherent soil properties which are the result of thousands of years of adaptation will not be altered appreciably by a superficial treatment applied over a comparatively short period of time. It has been pointed out earlier (fig. 2) that despite the different productivity of soils N and X (as a result of treatment) the relative incidence of the bacterial nutritional groups studied is very similar in both soils, an observation

which Taylor and Lochhead (5) have also made. Continuous planting of one crop may be expected eventually to stabilize the microbial balance of the soil and result in a microflora which is characteristic of that crop. Annual change of crop, as in rotations, however, will merely cause temporary shifts of the equilibrium (groups A and E in figure 1). Similarly, readily decomposable materials (dextrose) stimulate a temporary change in the equilibrium, which eventually reverts to its original state as a result of the powerful buffering capacity of the soil, whereas more slowly decomposable substances (cellulose) induce a shift of the bacterial balance which is not only more profound but also more persistent.

These considerations are especially important if it is desired to modify the soil population for a specific purpose such as the elimination of a disease factor from soil or the stimulation of a microflora favorable to a particular crop.

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